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Editorial

THE Journal of Chemical Physics which makes its appearance with this issue, is a natural result of the recent development of the chemical and physical sciences. At present the boundary between the sciences of physics and chemistry has been completely bridged. Men who must be classified as physicists on the basis of training and of relations to departments or institutes of physics are working on the traditional problems of chemistry; and others who must be regarded as chemists on similar grounds are working in fields which must be regarded as physics. These men, regardless of training and affiliations, have a broad knowledge of both sciences and their work is admired and respected by their co-workers in both sciences. The methods of investigation used are, to a large extent, not those of classical chemistry and the field is not of primary interest to the main body of physicists, nor is it the traditional field of physics. It seems proper that a journal devoted to this borderline field should be available to this group.

During the nineteenth century, atoms and molecules were the particular working concepts of chemists, but since the turn of the century, chemists and physicists have become equally serious students of atoms and molecules and the fundamental particles of which they are composed. New and effective methods, experimental and theoretical, for the study of these units from which massive matter is composed, have developed largely from physical discoveries which at the time did not appear to have the importance to century-old chemical problems that they have since assumed. The discovery of radioactivity has made great contributions to the structure of atoms; mathematical physics has contributed to many chemical problems such as the nature of solutions, the kinetics of reactions and the statistical interpretation of thermodynamics; the discovery and development of wholly new experimental methods have made possible a detail of knowledge which was previously impossible of attainment; and most important of all, the experimental and theoretical work associated with the quantum theory has made a profound contribution to our knowledge of chemistry and physics. Moreover, the history of these sciences in recent years teaches the effectiveness of applying the exact logic of mathematics to chemical as well as physical problems.

Those of us actively engaged in the founding of this journal, the American Institute of Physics, contributors, subscribers and editorial board, are doing so because of our interests in this borderline field and our belief that a journal devoted to this field will best serve those interests. The life and interests of the individual are short and of little consequence as compared to the lives of our sciences. These have gone on for centuries and will go forward for longer lengths of time. The life of a scientific journal should be comparable with that of the science it serves, or at least with the broad developments of that science. We hope that our journal has such a long, useful life.

Any statements on subject matter and editorial policy must of necessity be temporary in character. A research journal serves that narrow boundary between the known and unknown and though we may comprehend something of the past, the future developments can only be

guessed dimly for brief periods of time. We shall accept papers for publication which fit into the field of this journal as we see it at each moment. These will be criticized as impersonally as possible on the basis of experimental exactitude and logical reasoning. We hope the journal may build up a tradition of prompt publication of papers presented, realizing that once work is completed, no useful purpose is served by delay in publication; in fact, a saving of effort may often be made by prompt publication, since it helps to avoid duplication of work. Finally, we wish its editorial policies to be characterized by a flexibility which will enable it to follow the new and interesting developments of each year of its existence.

HAROLD C. UREY,
Managing Editor

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An Extension of the Phase Rule for Adsorption under Equilibrium and Non-Equilibrium Conditions

IRVING LANGMUIR, *General Electric Company*

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An *adsorption field* is defined as a homogeneous part of a solid or liquid surface on which adsorption can occur. In presence of adsorbable components each field contains one or more *surface phases*. Adsorption experiments have demonstrated that in many cases all the intrinsic properties of an isolated surface phase are variables characterized by $C+1$ degrees of freedom (F) where C is the number of components. If this *surface phase postulate* (S.P.P.) applies to each surface phase in a system, then, for a system in a state of complete equilibrium, F has the value $F_0=C+S-P_v-P_s+2$ where S, P_v and P_s are the numbers of fields, volume phases and surface phases, respectively. By considering the possible mechanisms, such as *interphase mobility* and *vapor interchange* by which equilibrium may be attained, this phase rule is extended to states of partial equilibrium, for example, cases where the surface phases and the volume phases are at different temperatures. The effects of electric fields are considered. Non-equilibrium states, which may be divided into *steady states* and *transient states* are characterized by values of F greater than F_0. Experiments on transients by which F can be determined may thus serve to determine S when it is otherwise unknown. If the geometrical arrangement of the surface phases is known, such experiments serve to determine the *surface diffusion coefficient* D, or the phase boundary resistance to diffusion. The applicability of the S.P.P. depends on a certain degree of *intraphase mobility* of the adatoms.

ADSORBED atoms or molecules[1] on the surface of a solid body tend to occupy definite positions (elementary spaces) which are determined by the crystal lattice of the solid or by the arrangement of its atoms if it is amorphous.[2]

Although at any instant of time nearly all the adatoms occupy equilibrium positions within the elementary spaces, thermal agitation causes them from time to time to hop from one space to an unoccupied adjacent space. This results in a mobility of the adatoms which manifests itself as a surface diffusion if the surface concentration is not uniform.

The finely divided or porous solids employed in most adsorption experiments usually contain many different types of elementary spaces so that the surface of the solid is to be regarded as heterogeneous. However, it must frequently happen that the adsorption actually observed takes place on only one of the several types of spaces present. Even with these heterogeneous surfaces we may thus sometimes be justified in regarding the surface as homogeneous.

The writer has long believed that compact surfaces of crystalline bodies, such as that of a well-aged tungsten filament, are to be regarded as essentially homogeneous surfaces in the sense that practically all the elementary spaces are alike. In some recent studies of the evaporation of atoms, ions and electrons from a tungsten filament in presence of caesium vapor in collaboration with Dr. J. B. Taylor, definite proof[3] has been obtained that such a tungsten surface is actually homogeneous except for the presence of isolated more active elementary spaces which cover only 0.005 of the surface.

The object of the present paper is to consider theoretically some of the fundamental properties of homogeneous surfaces and of heterogeneous surfaces which contain a finite number of different kinds of elementary spaces. Reference to experimental data will be made only to illustrate some of the concepts advanced. Applications of these principles will be made in a paper with J. B. Taylor which will soon be submitted to the *Physical Review*.

DEFINITION OF ADSORPTION FIELD

In the study of heterogeneous equilibria by the methods of Gibbs, the term *phase* is used to designate homogeneous parts of a system with-

[1] We shall use the word *adatom* in this paper to denote both adsorbed atoms and molecules.

[2] I. Langmuir, J. Amer. Chem. Soc. **40**, 1361–1403 (1918).

[3] I. Langmuir, J. Amer. Chem. Soc. **54**, 2798–2832 (1932). See especially p. 2829.

out regard to quantity or form. In a somewhat similar way let us introduce the concept of *field* to distinguish homogeneous parts of a surface on which adsorption can occur, which differ in structure or composition without regard to the size or shape of the areas involved. A simple example of a two-field system would be a surface consisting of two types of crystal faces, which, because of the differences in the surface lattices of the atoms, possess different properties. In general a single field consists of elementary spaces of only one kind.

It should be emphasized that the term field is used to denote a certain aggregation of elementary spaces and does not depend in any way on the presence or absence of adatoms in these spaces.

The surfaces of the tungsten filaments already referred to apparently contain two kinds of elementary spaces, *normal* and *active*. The active areas consist of isolated elementary spaces covering only 0.005 of the total surface, each active space being surrounded by normal spaces. In this case we may regard the surface as consisting of two fields, one *continuous field* (normal) and one *disperse field* (active). In some cases we shall see that we may be justified in applying the concept of field to a surface containing two or more kinds of elementary spaces if these are sufficiently uniformly dispersed over the surface and if the interchange of adatoms between the spaces (mobility) is sufficiently rapid to bring about equilibrium between them.

We shall use the symbol S to denote the number of fields present in any system.

Surface Phases

When a substance is adsorbed on a surface consisting of one or more fields, there will be within each field one or more surface phases. A *surface phase* may be defined as a homogeneous part of a system which extends over a surface field or over a part of a field which is separated from other parts by a boundary. In general, a surface phase consists of an incomplete monatomic film of adatoms; this, however, does not need to be assumed in the following discussion.

In the classical treatment of heterogeneous equilibria the term *phase* is given significance only in systems which are in a state of complete equilibrium. Experiments on adsorption of Cs, Th, and oxygen on tungsten filaments have convinced the writer that in dealing with surfaces this concept of phase may be very profitably generalized to include non-equilibrium conditions.

The essential element in the concept of phase is that the properties of each phase are characterized by a definite number of parameters or degrees of freedom. Experiments have shown that in a large number of cases the properties of adsorbed films are characterized by a definite number of parameters even under non-equilibrium conditions. There are, of course, some cases (to be discussed later) where experiments show that under non-equilibrium conditions the number of degrees of freedom characterizing a single adsorbed film is greater than when this film is brought to equilibrium. In such cases the concept of surface phase cannot be applied. We are, however, justified in using the concept of phase whenever the adsorbed film conforms to the following postulate.

Surface Phase Postulate

All the intrinsic properties of a surface phase possess $C+E+1$ degrees of freedom even under non-equilibrium conditions. Here C represents the number of components in the system in the same sense as is used in the phase rule. We must not count as components the substances needed to provide the fields; thus the tungsten on which adsorption occurs is not one of the components. The symbol E is used to denote the degree of freedom corresponding to the application of an external electric force to the surface field. In the adsorption of such substances as Cs an electric field of a few thousand volts per cm causes very appreciable changes in the rates of evaporation of ions and electrons so that it seems desirable in many cases to include the electric force as one of the independent variables in the system. For a single surface phase exposed to an electric field we thus put $E=1$, but if we do not permit the electric field to vary we may put $E=0$, in accord with ordinary usage.

In the above postulate, by degrees of freedom we mean the number of independent parameters needed to fix the properties of the phase. We may, for example, take the independent variables to be temperature T, the electric field, and the surface concentrations σ_1, σ_2, etc., corresponding

to each of C components (σ = adatoms per cm^2). When the values of these $C+E+1$ variables are chosen, all other properties, such as contact potential, rates of evaporation of each component, surface spreading force f (two-dimensional analog of the pressure) etc., are fixed.

It must be recognized that the validity of the surface phase postulate (hereafter referred to as S.P.P.) depends upon a certain amount of mobility of the adatoms, at least under non-equilibrium conditions. This may be illustrated by the following model. Let us assume that *under equilibrium conditions* the adatoms are distributed uniformly among the elementary spaces in the field. By this we mean that not only is the probability that a given space is occupied, the same as that any other space is occupied, but also that the probability that any space is occupied is not altered by the occupation of neighboring spaces. We shall call this the *normal* distribution. Such a distribution implies that there are no forces between adatoms except those needed to keep two adatoms from occupying the same space. We may imagine this normal distribution to have been brought about by interchange with a vapor phase without the necessity of surface mobility. If the distribution is changed in any way from the normal, it will return exponentially to normal through the vapor phase at a rate characterized by a time of relaxation τ_v. It is obvious that the properties of the absorbed film in the final normal state depend only on σ and T (assuming the surface field and the electric condition to have been given).

Let us now consider non-equilibrium conditions, particularly during the building up of the film from $\sigma=0$ to its final value σ_∞ by condensation from the vapor phase. If, by momentarily raising the pressure in the vapor phase, the rate of arrival of atoms on the surface is made so high that the surface concentration reaches σ_∞ in a time very short compared to τ_v, there is no necessity of assuming that the normal distribution will have been reached when $\sigma=\sigma_\infty$. As long as only a small fraction of the surface is covered by adatoms, the incident atoms will have a random or normal distribution. But when σ becomes so high that an appreciable fraction of the incident atoms strike adatoms, there will tend to be a clustering of adatoms on the surface. Let us assume, for example, that when an incident atom is following a path which would bring it to a space already occupied, it slides or hops to the nearest unoccupied space in the field.[4] If there is no surface mobility of adatoms already in elementary spaces, this mechanism of condensation results in a distribution in which the probability that a given space is occupied is increased by the occupancy of neighboring spaces, so that the distribution is not normal. Surface mobility, if present, would cause the distribution to return towards normal with a time of relaxation τ_s. In order to obtain the abnormal type of surface distribution it is thus only necessary that the time of condensation shall be small compared to both τ_v and τ_s.

If the conditions permit the distribution to be abnormal in this sense, we see that the properties of the adsorbed film should in general be dependent on other factors than σ and T, that is, should have more degrees of freedom than $C+E+1$ and the S.P.P. would not be applicable.

Thus the S.P.P. holds for transient conditions only if the duration of the transient states is large compared to τ_s, the relaxation time for surface mobility. The S.P.P. is thus rigorously true only for equilibrium conditions, but experiments have shown that it is so frequently applicable with high accuracy that its use is justified.

Before attempting to calculate the number of degrees of freedom of a system consisting of any number of surface and volume phases, let us consider a simpler system.

An Example of Two Surface Phases in a Single Field

When a tungsten filament is surrounded by a negatively charged cylinder in presence of a definite pressure of Cs vapor, there is a critical temperature at which the adsorbed film of Cs on the filament consists of two surface phases.[5,6] In one of these phases (α) the surface concentration

[4] Evidence that this happens in the case of Cs and W will be presented in a forthcoming paper by J. B. Taylor and the writer.

[5] I. Langmuir and K. H. Kingdon, Science **57**, 58–60 (1923).

[6] I. Langmuir and J. B. Taylor, Phys. Rev. **40**, 463 (1932).

is extremely low[7] ($\theta \sim 0.001$) and the Cs evaporates from it almost wholly as positive ions, while the other phase (β) is of much higher concentration ($\theta \sim 0.15$) and Cs evaporates from it only as atoms. There is a relatively sharp boundary (0.05 cm wide at 1000°K) between the phases.

Thus with a Cs pressure of 9.2×10^{-4} baryes, corresponding to saturated Cs vapor at a bulb temperature $T = 291$°K, the rate of arrival μ of Cs atoms on the surface is 1.24×10^{14} atoms cm^{-2}. Under these conditions with a potential of -45 volts on the cylinder the two surface phases are in equilibrium when the filament temperature T_0 is 1027°. If the filament temperature is raised above T_0, the boundary moves in such a way as to cause the disappearance of the β phase. At any given temperature, T, more than a few degrees above or below T_0, the boundary moves with a uniform velocity v which varies in proportion to $T - T_0$ so that $v = 9.0 \times 10^{-4}(T - T_0)$ cm sec.$^{-1}$. The critical temperature T_0 at which $v = 0$ varies slightly with the strength of the accelerating field acting on the escaping ions; an increase in the field causes a lowering of T_0. Changing the Cs pressure from 9.2 to $16.3(\times 10^{-4})$ baryes by raising the bulb temperature 4° increases T_0 from 1027° to 1052°.

It is clear that this system is one involving two volume phases (the solid Cs on the walls of the tube, and the vapor phase) and two surface phases (α and β). Of course the system is not in any sense in thermodynamic equilibrium for the volume phases and the surface phases are at different temperatures and the Cs atoms which go on to the filament as neutral atoms leave it partly as positive ions. Nevertheless the system conforms perfectly to the extension of the phase rule which we shall derive in the following pages.

The system is one possessing 3 degrees of freedom ($F = 3$). For example, if we choose definite values for the bulb temperature T_B, the filament temperature T and the electric field, the properties of both surface phases are fixed and even the velocity of movement of the boundary is fixed. Under these conditions the two surface phases can only coexist for a short time. If we impose the condition that the two surface phases shall coexist permanently, as though in equilibrium, we require that $v = 0$ and there are then only 2 degrees of freedom. For a definite value of the electric field there remains only 1 degree of freedom; thus there is only one filament temperature for each bulb temperature (or Cs pressure). If the Cs vapor is not saturated at the bulb temperature, there is only one volume phase instead of two and there is then an additional degree of freedom: the bulb temperature and the Cs pressure are both independent variables.

Let us analyze more closely how the coexistence of the two surfaces phases fixes F. Consider the system consisting of the vapor phase and the two surface phases in a single field. There is one component (Cs), or $C = 1$. Assuming that the accelerating field is fixed, the S.P.P. gives 2 degrees of freedom for each surface phase and since there are 2 degrees of freedom for the vapor phase there is a total of 6 degrees of freedom. We must now subtract the degrees of freedom defined by the system itself.

The two surface phases must be at the same temperature: $T_1 = T_2$. The permanent coexistence of the two phases requires that the rate of supply of Cs to each phase from the vapor shall equal the rate of evaporation from that phase. Let ν_a and ν_p be the rates of evaporation of atoms and of ions (atoms or ions cm^{-2} sec.$^{-1}$) from a surface phase, then the total rate at which Cs atoms (nuclei) leave the surface is

$$\nu = \nu_a + \nu_p. \tag{1}$$

To maintain a steady state the values of ν for the two surface phases must both equal μ, the rate of arrival from the vapor phase. Thus we have the two conditions $\nu_1 = \mu$ and $\nu_2 = \mu$.

These, with the conditions for temperature equality, $T_1 = T_2$, reduce F from 6 to 3.

There is also a *phase boundary condition* which must be fulfilled if the two phases are to coexist. Between the phases there must be a boundary of finite width in which the surface concentration varies continuously from σ_1 to σ_2, the concentrations of the phases. The total rate of evaporation ν in a definite accelerating field for ions is a function of σ and T which rises from 0 at $\theta = 0$ to a sharp maximum at about $\theta = 0.01$, falls to broad minimum at $\theta = 0.08$ and then rises continuously. There are thus in general three values of θ which

[7] The covering fraction θ is defined as the ratio σ/σ_1 where σ_1 is the surface concentration of a complete monatomic film, 3.56×10^{14} atoms cm^{-2} for Cs on W.

fulfill the condition $\nu=\mu$. The two extreme values θ_1 and θ_2 represent stable or at least metastable equilibrium, while the intermediate value θ_M corresponds to unstable equilibrium. At points within the boundary transition where θ varies from θ_1 to θ_M, $\nu>\mu$ so that Cs evaporates faster than it arrives from the vapor phase. In the region between θ_M and θ_2, on the other hand, the Cs condenses faster than it evaporates. For a steady state the excess Cs must migrate on the surface from the latter region to the former.

If D, the surface diffusion coefficient, can be taken to be independent of θ, the laws of diffusion thus require that

$$\nu-\mu=D(d^2\sigma/dx^2), \tag{2}$$

where x is a distance measured in a direction perpendicular to the phase boundary. Multiplication of both sides of this equation by $d\sigma$ and integration between the limits θ_1 and θ_2 gives the condition (since $d\sigma/dt$ is zero at $\theta=\theta_1$ and at $\theta=\theta_2$)

$$\int_{\theta_1}^{\theta_2}(\nu-\mu)d\theta=0. \tag{3}$$

This then is the required *phase boundary condition*. This reduces the number of degrees of freedom from 3 to 2 giving a result in accord with the experimental observations.

Phase Rule for Equilibrium between P_v Volume Phases and P_s Surface Phases in S Fields

Let us assume that the electric fields are either zero or have a definite value so that $E=0$. Each volume and surface phase, if isolated from the others, has $C+1$ degrees of freedom in accord with the S.P.P., giving for the P_v+P_s phases the total number of degrees of freedom

$$F_N=(P_v+P_s)(C+1). \tag{4}$$

When the phases are brought together in a single system, we must subtract the degrees of freedom which are defined by the system itself. For true equilibrium the equilibrium conditions are of four types:

(1) Temperature equilibrium

All P_v+P_s phases must have the same temperature. This gives P_v+P_s-1 conditions.

(2) Pressure equilibrium among the volume phases: P_v-1 conditions

(3) Spreading force (f) equilibrium between the surface phases in any one field

There is no need for f to have the same value for surface phases in different fields since the boundaries of the fields can withstand differences of spreading force. But two or more phases in any one field must all have the same value of f for true equilibrium. This requirement fixes P_s-S conditions.

(4) Concentration equilibrium

According to Gibbs a true thermodynamic equilibrium requires that the chemical potential of each component shall be the same in all phases. This fixes $(P_v+P_s-1)C$ conditions.

If all four sets of equilibrium conditions are fulfilled we have a total of $(P_v+P_s-1)(C+2)-S$ variables that are defined by the system.

Subtracting these defined variables from the total F_N given by Eq. (4) leaves for F_0 the degrees of freedom for the whole system under equilibrium conditions

$$F_0=C+S-P_v-P_s+2. \tag{5}$$

This reduces to the ordinary phase rule if we put $S=P_s=0$.

Non-Equilibrium States

Non-equilibrium states are of two kinds: *steady states*, in which the intrinsic properties of all phases and the relative amounts of the phases do not vary with time and *transient states* in which at least one of these variables changes with time. We shall attempt to consider only types of non-equilibrium states which are of practical importance in studies of adsorption phenomena. In general, we shall deal with systems in a state of *partial equilibrium*, for example, systems in which all the phases within a group of phases are substantially in equilibrium with one another although they may not be in equilibrium with other phases present.

We shall confine ourselves to cases in which the S.P.P. applies to each surface phase and shall assume that a corresponding volume phase postulate holds for the volume phases. We have seen that this is equivalent to postulating that

intraphase equilibrium (i.e., within each phase) exists at all times because of surface mobility.

Let us now consider in turn the mechanisms of equilibrium attainment corresponding to the four types of equilibrium listed in the previous section.

(1) Partial thermal equilibrium

Temperature gradients in otherwise homogeneous solids or liquids are common enough, but sharp temperature discontinuities at the boundaries between phases are not ordinarily encountered. However, if the pressure in a vapor phase is so low that the mean free path of the molecules is large compared to the dimensions of a surface (for example, the diameter of a filament) in contact with it, it is possible to have the vapor phase at a temperature which is very different from that of the surface. Such conditions are highly advantageous for the study of adsorption phenomena[8] since the rate of arrival of atoms μ is then accurately known from the bulb temperature and the vapor pressure according to the equation

$$\mu = p(2\pi mkT)^{-1/2} = 2.652 \times 10^{19} p(MT)^{-1/2} \text{ molecules cm}^{-2}\text{ sec.}^{-1}, \quad (6)$$

where M is the molecular weight. In general, therefore, we shall assume that the surface phases are all at one temperature T_s, while the volume phases are at the temperature T_v.

(2) Pressure equilibrium

We shall assume that this equilibrium between the volume phases is always complete.

(3) Partial spreading force equilibrium

The equilization of spreading force f in different phases within one field may take place in 3 ways:

(*a*) *Interphase mobility* by which adatoms cross the phase boundary. The rate of interchange may in general be limited by the rapidity of surface diffusion within the phase (in which case the S.P.P. cannot be strictly applicable) or by a *phase boundary resistance*, as if, for example, the adatoms had to pass from one surface phase to the other across the bounding line by a process analogous to evaporation or condensation.

(*b*) *Vapor interchange* by evaporation into and condensation from the vapor phase. The mechanism of this process will be discussed in the following section.

(*c*) *Phase boundary displacement.* Without migration of adatoms across phase boundaries and without vapor interchange, the surface concentration and therefore f may vary because of a change in the relative areas of the phases within a field.

All three mechanisms, if undisturbed by other factors, must, of course, lead to identical equilibrium states, but the time of relaxation corresponding to the 3 mechanisms may be very different.

In the case of the non-equilibrium states observed with Cs on W with an accelerating field for ions, the two phases are not in spreading force equilibrium, but the coexistence of the two phases depends on a relation like that expressed by Eq. (3). During movement of the phase boundary the particular form of this equation becomes modified, but in its modified form it still acts to reduce the number of independent variables just as if we postulated spreading force equilibrium.

A substitution of a *phase boundary condition* for a *spreading force equality* condition leaves the number of degrees of freedom unchanged.

(4) Partial concentration equilibrium

Again we have the 3 mechanisms of interphase mobility, vapor interchange and boundary displacement for the attainment of equilibrium. In this case we may, however, have partial equilibrium in the sense that equilibrium is reached only in regard to certain components. Or, only certain of the phases may be in equilibrium with one another.

For complete equilibrium we have seen that the chemical potentials for each component must be equal in all phases. But for phases which are not at the same temperature this condition is not applicable. It is also not applicable to the α and β phases observed with accelerating fields for ions, since these two phases are not in true thermodynamic equilibrium. We may, however, still employ the chemical potentials to define equilibria among surface phases by the mechanisms of interphase mobility and boundary displacement since we have postulated that these surface phases are all at temperature T_s.

For the mechanism of equilibrium attainment by vapor interchange we may replace the rule of equality of chemical potentials by the following.

[8] I. Langmiur, J. Amer. Chem. Soc. **37**, 1139–1167 (1915).

Criterion for Concentration Equilibrium through Vapor Interchange

Any surface phase is in concentration equilibrium with the vapor phase if

$$\nu=\alpha\mu \tag{7}$$

holds for each component.

Here α, the condensation coefficient, is a pure number which cannot exceed unity and in fact often equals unity. In any case, by the S.P.P. both α and ν are intrinsic properties of the surface phase and as such possess $C+1$ degrees of freedom. We assume that there is only one vapor phase and that all the surface phases are in contact with it. There are then P_sC conditions furnished by the criterion for concentration equilibrium, the same number as would be given by the chemical potentials. The mechanism of vapor interchange is thus capable of bringing the P_s phases to a state of complete equilibrium with the vapor phase.

Interphase Mobility

This concentration equilibrium between surface phases may, however, also be brought about by mobility of adatoms. Consider, for example, three surface phases A, B, C, each of which is in contact with the two others while all three are in contact with the vapor phase V. Each line of contact between the surface phases provides a mechanism by which concentration equilibrium may be attained; there are then six mechanisms where only three are essential. Corresponding to each of the six contacts between phases, which can be represented by VA, VB, VC, AB, BC and CA, there is a relaxation time τ_{VA}, τ_{VB}, etc.

Suppose the concentration of one of the surface phases, say A, is altered so that the phase is not in equilibrium with the others in contact with it. The return to equilibrium occurs primarily through the three mechanisms VA, AB and CA. If the three relaxation times τ_{VA}, τ_{AB} and τ_{CA} are very different from one another, the rate at which A returns to equilibrium depends on the fastest of the three processes; the other two may be entirely insignificant in their effect.

Consider a case where τ_{AB} is very small compared to the other five τ's. Then A and B remain substantially in equilibrium with one another, even when they are not in equilibrium with V and C. In such cases we may say that the interphase mobility between A and B is *complete* while that between A and C is *incomplete*. Similarly we may describe the vapor interchange as being complete or incomplete.

Degrees of Freedom in Non-Equilibrium States

We have seen that for complete equilibrium the four sets of equilibrium conditions fix $(P_v+P_s-1)(C+2)-S$ variables leaving F_0 degrees of freedom as given by Eq. (5). For partial equilibrium a definite number, say ΔF, of the foregoing equilibrium conditions are not fulfilled. This gives then for F, the number of degrees of freedom of the entire system, the value

$$F=F_0+\Delta F. \tag{8}$$

If the system is a closed system, it will ultimately reach a state of true equilibrium, although, of course, the rate of approach to this state may be very slow. Thus the ΔF additional degrees of freedom cause transient phenomena to occur in any closed or isolated system. The transient states may be said to be characterized by ΔF degrees of freedom.

If $\Delta F>0$ the system can be maintained in a steady state only by providing it with ΔF independent steady power sources and the system is then no longer a closed system.

If, after having maintained the system in a steady state by these ΔF sources, we cut off some of these sources so that only W power sources remain, the transient states that then occur are characterized by $\Delta F-W$ degrees of freedom provided that ΔF is unchanged by cutting off the energy supply.

Effects of Electric Fields

If the surface phases are all exposed to the same variable electric field, we must increase F_0 as given by Eq. (5) by one unit. However, with true equilibrium we can have a homogeneous vapor phase in presence of an electric field only if no charged particles are present, that is, only if the surface phases emit neither electrons nor ions. If such particles are emitted, we have as a fifth condition for equilibrium the absence of electric field. Whenever an electric field produces

a flow of current from a surface, the effect of the field is to increase ΔF by one unit.

A steady electric field with surfaces that emit ions or electrons requires a source of electric power. We can have electric fields in an isolated system only if the system includes a device, such as a charged condenser, which can store electrical energy. In such a closed system, the additional degree of freedom corresponding to the field appears as an extra degree of freedom characterizing the transients, for example, the electric field will vary with time.

Let us now illustrate the applications of Eqs. (5) and (8) by examples chosen from the experiments with tungsten filaments in presence of Cs vapor.

Case I. Steady states in atom evaporation

A tungsten filament is maintained at a temperature T_s (400° to 1200°K) in a bulb containing metallic Cs at a temperature T_v (240° to 270°K). After a steady state has been reached (1–30 minutes) the fraction θ of the surface of the filament covered by a monatomic layer of Cs atoms is determined.[9] The experiments have shown that for any given values of T_s and T_v, θ always has the same value, that is, θ is a function of T_v and T_s only. The system is thus one which possesses 2 degrees of freedom or $F=2$.

The experimental data are ordinarily used to derive an expression giving μ as a function of θ and T. It is, of course, permissible to use any two variables characteristic of the system as independent variables and to take any other variable as dependent variable. All the properties of the surface phase such as ν_a, ν_p, ν_e (evaporation rates of atoms, ions or electrons) are thus expressible as functions of θ and T in accord with the S.P.P.

The system is of one component (Cs) and contains two volume phases (vapor and metallic Cs), one surface field and one surface phase. Putting $C=1$, $P_v=2$, $S=1$ and $P_s=1$ in Eq. (5) we find $F_0=1$ for a state of true equilibrium. We have, however, only partial equilibrium since $T_v \neq T_s$; the other equilibrium conditions for pressure and concentration are fulfilled. Therefore we have $\Delta F=1$ and by Eq. (8) $F=2$ in agreement with the experimental observations.

[9] I. Langmuir, J. Amer. Chem. Soc. **54**, 1252 (1932).

To maintain the filament at the temperature T_s we must supply heat to the filament (electric power) at a steady rate. This one source of power corresponds to $\Delta F=1$. If we stop the current flow to the filament, the transient states that then occur are characterized by one degree of freedom *provided* that ΔF is still unity. This will be the case if during the cooling of the filament, the vapor interchange is complete so that the concentration equilibrium condition continues to be fulfilled. With small filaments, however, the rate of cooling will usually be so rapid that concentration equilibrium between the vapor and the surface phase will not be maintained (i.e., vapor interchange is incomplete) so that an additional degree of freedom is introduced. The transients would then be characterized by two degrees of freedom. With only one degree of freedom any property of the filament is given as a function of time by a single curve; differences in initial temperature correspond merely to a displacement of the curve parallel to the time axis. With two degrees of freedom a family of curves would be needed to represent these transients and these could not be made to coincide by a mere displacement along the time axis.

Case II. Steady states in ion and electron evaporation

A potential difference V is applied between the filament and the bulb, the surface of which is made conducting by a film of platinum. Since the filament is capable of emitting either electrons or ions, the condition for true equilibrium if only one surface phase is present requires that $V=0$ and thus, as in case I, $F_0=1$. On the other hand, with partial equilibrium, because of the electric field we find $\Delta F=2$ so that $F=3$.

Experimentally we find, in fact, three degrees of freedom for this system. The bulb and filament temperatures and the voltage V may be given any values, but then the rate of evaporation of ions or electrons is fixed. Actually the effect of increasing the field is to increase even the "saturation" currents of ions or electrons very considerably.

When two surface phases appear, F is reduced from 3 to 2 so that, as independent variables we may have T_v and V; T_s can be considered to be the dependent variable.

Case III. Transients in atom evaporation

If the filament temperature is suddenly changed, θ, and all other properties of the surface phase, change with time until finally a new stationary state is asymptotically reached. During this transition there are two equilibrium "conditions" that are not fulfilled: *viz*, there is neither thermal nor concentration equilibrium. Thus $\Delta F=2$ and $F=3$. If the filament temperture is maintained by the proper energy supply, the transients are characterized by one degree of freedom. The experimental data agree with this conclusion, thus indicating that the S.P.P. is fulfilled even during these transient states.

Degenerate Surface Phases

Consider a system which contains S fields each containing one surface phase so that $P_s=S$. Then by Eq. (5)

$$F_0=C-P_v+2. \tag{9}$$

Experiments with systems in states of complete equilibrium can be used to determine F_0, but since S and P_s are not contained in Eq. (9), this cannot be used to obtain information regarding the number of surface phases.

It may often be possible, however, from experimental studies of non-equilibrium states to get data from which S may be found. For example, suppose that no two of the S surface phases are in concentration equilibrium with one another and only one surface phase is in equilibrium with the vapor phase. Then $(S-1)C$ conditions, which would be required for concentration equilibrium, are not fulfilled. We may also assume that $T_s \neq T_v$. Thus we have $\Delta F=C(S-1)+1$ and by Eqs. (8) and (9), $F=CS-P_v+3$.

An experimental determination of F thus furnishes knowledge of S.

Since complete interphase mobility between any two phases decreases F by C units, its effect on F is the same as if one surface phase disappeared. We thus have the theorem:

> Two phases at the same temperature which are maintained in concentration equilibrium by interphase mobility behave as a single phase in determining the number of degrees of freedom of any system of which they form a part.

A corollary of this theorem derivable from Eq. (7) is:

> The values of ν/α (for each component) are the same for two surface phases at the same temperature if these phases are in concentration equilibrium through interphase mobility.

The Degree of Surface Mobility Needed to Maintain Equilibrium between Surface Phases

Consider two surface phases which are in concentration equilibrium with one another but are not in equilibrium with the vapor phase; that is, the value of ν/α, which is the same for both phases, is not equal to μ. In general, the maintenance of concentration equilibrium between the phases then requires a flux of adatoms across the phase boundaries, but this must occur without any appreciable concentration gradient.

Let us consider, for example, the transient states that occur if the concentration of a vapor phase, which was previously in equilibrium with two surface phases, is suddenly reduced to zero so that $\mu=0$. The differential equation for the diffusion of the adatoms in each surface phase is then

$$\partial\sigma/\partial t+\nu=D(\partial^2\sigma/\partial x^2+\partial^2\sigma/\partial y^2), \tag{10}$$

where D is the surface diffusion coefficient. For simplicity in illustrating the applications of this equation, consider the one dimensional problem arising if one of the phases consists of strips of width b. Let us neglect the term $\partial\sigma/\partial t$. The drop in concentration between the center of the strip and the phase boundary forming the edges of the strip is then

$$\Delta\sigma=\nu b^2/(8D). \tag{11}$$

The condition for concentration equilibrium is that $\Delta\sigma$ shall be negligibly small compared to σ or

$$\nu b^2 \ll 8D\sigma. \tag{12}$$

With any given value of D we see that the equilibrium between surface phases is maintained most readily when the size of the areas occupied by the phase is small.

An equivalent statement of the criterion for surface phase equilibrium is that the time of relaxation corresponding to interphase mobility shall be negligible compared to that for vapor interchange.

The experiments with Cs films on W have

shown, by different methods from those here described, that the average life of Cs adatoms on certain *active* areas, which cover only 0.005 of the surface, is about 4000 times (at 1000°K) longer than it is for adatoms on the normal part of the surface. We thus conclude that there are two surface fields and two surface phases.

If there were no surface mobility, it is clear that during the building up of a surface film by slow condensation from the vapor phase, the surface concentration σ_a and σ_n in the two phases would remain equal until evaporation causes them to approach equilibrium. On the other hand, if a composite film having the same total Cs content were formed by evaporation from a film which had previously reached equilibrium with a more concentrated vapor, the value of σ_a corresponding to the disperse phase would be far higher than that for the continuous phase because of the longer life of the adatoms in the active areas.

Thus the rate of evaporation from the composite surface would depend not only on T_s but on σ_a and σ_n and so involves three degrees of freedom.

A degree of mobility, however, sufficient to maintain equilibrium between the two phases imposes a definite relation between σ_a and σ_n at any given temperature and thus reduces F to 2.

Experiments on transients[10] were carried out with very low surface concentrations when about half of the total Cs content of the surface was in the disperse or active phase. The results showed unmistakably only two degrees of freedom. From the data thus obtained (taking $D=1.4\times10^{-4}$ cm^2 sec.$^{-1}$ at 970°K given by other experiments) it can therefore be concluded from Eq. (12) that $b<0.06$ cm. This means that the distances which adatoms must move within the areas covered by the normal phase before reaching the active spots are on the average not greater than about 0.03 cm. Other evidence has already indicated that the disperse phase consists of areas of approximately atomic dimensions probably located along crystal boundaries. Since microscopic examination showed the size of the tungsten crystals to be approximately 0.001 cm, it is not surprising that the two phases behave as a single phase during these transient states.

[10] To be published in *The Physical Review*.

Conditions which Determine Whether One or Two Surface Phases Exist in a Field

In general, for each component and for each phase we may express ν as a function of θ and T. Usually ν increases continuously so that θ is a single valued function of θ. It may happen, however, that ν has a maximum value at some value of θ and a minimum at some higher value with a point of inflection between the two. In such cases two phases may appear. The conditions necessary for the instability of a single phase which leads to the appearance of two phases may be obtained as follows:

Consider that a surface phase is in concentration equilibrium with a vapor phase so that $\nu=\alpha\mu$. This equilibrium may be stable or unstable. Suppose we produce a small variation δ in the value of σ from its equilibrium value σ_0. Then the differential equation to be satisfied is

$$\partial\delta/\partial t+\delta(\partial\nu/\partial\sigma)=D(\partial^2\delta/\partial x^2+\partial^2\delta/\partial y^2).$$

A particular one-dimensional solution of this equation is $\delta=\delta_0 \sin(2\pi x/b)e^{\gamma t}$, where

$$\gamma=-\partial\nu/\partial\sigma-4(\pi^2/b^2)D.$$

If γ is negative, the disturbance δ tends to die down so that the equilibrium is stable, but for $\gamma>0$ the equilibrium is unstable since δ increases with time. The condition for the development of *two phases* is thus $4\pi^2(D/b^2)<-\partial\nu/\partial\sigma$.

Thus it is not merely necessary that $\partial\nu/\partial\sigma$ shall have a negative value in order to have phase instability, but D/b^2 must be small.

It is intended in further experiments with tungsten filaments in 2-component systems (Cs and oxygen) to produce surface fields on opposite sides of a filament and thus by observations of transient states obtain measurements of D and of the properties of the two surface phases.

The principles outlined in the preceding pages are applicable in many cases to adsorbed films or the surfaces of liquids. Oil films on water are familiar examples of systems that may exhibit two or more surface phases. Experiments show cases in which the S.P.P. is fulfilled. In other cases marked hysteresis effects are observed of a kind which indicate that the S.P.P. does not apply, so that our extended form of the phase rule cannot be used.

A Method for the Determination of the Mass of Electrolytic Ions

P. DEBYE, *University of Leipzig, Leipzig, Germany*

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I.

THE question how many molecules of a solvent are intimately connected with the different ions in a solution is far from being solved. It occurred to me that we could perform some improvement if a method could be found enabling us to determine directly the masses of ions. Ordinarily the mass does not enter at all in our considerations and the reason is that the forces due to the friction of the ions in the solvent are so much larger than the dynamical reactions due to the masses. For an ion moving with a velocity v in a liquid, the frictional force may be put equal to ρv and the factor ρ is (for water as a solvent) of the order of magnitude 2.10^{-9}, as the friction is comparable to that of a sphere of radius 10^{-8} cm, according to Stokes' formula. On the other hand, the dynamical reaction due to acceleration is $m(dv/dt)$ if m is the mass of the ion. If therefore we consider an ion in a field of high frequency ω (number of vibrations in 2π sec.) the dynamical coefficient to be compared with ρ is ωm. In order to make this coefficient equal to ρ for an ion of the mass of an hydrogen atom ($1.64.10^{-24}$ g), the frequency would have to be equal to approximately $\omega = 10^{15}$ and for a mass a hundred times larger, we would still find $\omega = 10^{13}$. This means that mass effects such as we are considering here would not become important in comparison with friction effects except in the infrared region. However, in this region considering ordinary solutions in water as an example, it is doubtful if measurements of the absorption coefficient of infrared waves would give much information, as the proper absorption of the water itself will be important. That is why I tried to look for an effect, which is zero as long as the dynamical reactions of the ions are neglected and would therefore provide us with a direct measurement of these reactions alone. Suppose we introduce supersonic waves in a solution of an electrolyte. If then only frictional forces should exist between the ions and the solvent, there will be no difference between the velocity of the ions and the velocity of the surrounding liquid. The solution will behave like a homogeneous liquid. If, however, the dynamical reactions are taken in account, these reactions will be different for ions of different masses. As a result, the motion, say of the positive ions, may differ from that of the negative ions. But this means that periodically changing electric charge densities will accompany the sound waves. That is why we should expect potential differences of the period of the sound waves set up between different points of an electrolyte solution by the passing of sound waves. It is obvious that if we can detect and measure this effect, we will be able to draw definite conclusions as to the masses of the ions and in this way as to the number of solvent molecules connected with them.

II.

It remains first of all to be seen what the magnitude of the presumed effect will be. For this purpose the following calculation is presented. No account is taken of interionic attraction, but I think that we may safely wait for the experiments to be performed first as no fundamental change in the results is to be expected from this improvement, although the absolute value of the effect will be influenced especially for higher concentrations.

Suppose the solution contains per cc: $n_1, n_2, \cdots n_i, \cdots$ ions of charges $e_1, e_2, \cdots e_i, \cdots$ with the friction constants $\rho_1, \rho_2, \cdots \rho_i \cdots$ and the masses $m_1, m_2, \cdots m_i \cdots$. If at a certain moment, t, and in a certain place, which we will characterize by one single variable, x (only considering plane waves going in the direction x), the velocity of the solvent is v_0 and the velocity of the ions are $v_1, v_2, \cdots v_i, \cdots$ we have a first set of equations of the form

$$e_i X - \rho_i(v_i - v_0) = m_i(dv_i/dt). \qquad (1)$$

They are equal in number with the number of

different ions contained in the solution and express that in every moment the total force acting on one ion has to be equal to its mass times its acceleration. The force on the left-hand side of (1) is made up of two parts, one part e_iX due to the electric component X of the forces, which in turn will be due to the electric charges in the solution, provided such charges appear. The other part, $-\rho_i(v_i-v_0)$ is the frictional force, which will result as soon as there is a difference between the actual velocities of the ion and the surrounding liquid.

A second set of as many equations as the number of different ions present is furnished by the equations of continuity, expressing that the gain in number of ions contained in an element of volume can only be due to ions entering or leaving through its surface.[1]

$$\frac{\partial n_i}{\partial t}+\frac{\partial}{\partial x}(n_iv_i)=0. \tag{2}$$

Calling the number of different ions z, we have now $2z$ equations for $(2z+1)$ variables, namely z numbers $n_1, n_2, \cdots n_i, \cdots$; z velocities $v_1, v_2, \cdots v_i \cdots$, and one additional variable, the field strength X. We make up for this deficiency in adding Poisson's equation, which has the form

$$D\frac{\partial \mathrm{X}}{\partial x}=4\pi\sum_j n_je_j \tag{3}$$

if D is the dielectric constant of the solvent.

III.

In order to solve these equations for the case in consideration, we assume

$$v_0=a_0e^{i(\omega t-kx)}. \tag{4}$$

If g is the velocity of the sound waves, we have

$$k=\omega/g=2\pi/\Lambda \tag{4a}$$

denoting with Λ the wave-length of the sound waves in the liquid.

The number of ions per cc n_i, will always be very nearly equal to its equilibrium value n_i. We put

$$n_i=\bar{n}_i+\nu_i \tag{5}$$

and try the assumption

$$\nu_i=\alpha_ie^{i(\omega t-kx)} \tag{5a}$$

with the unknown values of the α_i.

At the same time we assume

$$X=Ae^{i(\omega t-kx)} \tag{6}$$

with a value of A which is also unknown and has to be determined.

Considering the two facts that ν_i is very small compared with $\bar{n}_i$ and that $\Sigma\bar{n}_je_j=0$, our equations take the form

$$\begin{cases} e_iX-\rho_i(v_i-v_0)=m_i(\partial v_i/\partial t). \\ \partial\nu_i/\partial t+\bar{n}_i(\partial v_i/\partial x)=0. \\ D(\partial \mathrm{X}/\partial x)=4\pi\sum_j \nu_je_j. \end{cases} \tag{7}$$

Here moreover $\partial v_i/\partial t$ has been written instead of dv_i/dt, which is admissible as long as the velocities can be considered as small.

By introducing our special assumptions about the disturbance as due to a sound wave, the Eqs. (7) become

$$\left.\begin{array}{l} e_iA-\rho_i(a_i-a_0)=i\omega m_ia_i \\ i\omega\alpha_i-ik\bar{n}_ia_i=0 \\ -ikDA=4\pi\sum_j e_j\alpha_j \end{array}\right\}. \tag{8}$$

Combining the last equations of (8), we find

$$A=i(4\pi/D\omega)\sum_j\bar{n}_je_ja_j \tag{9}$$

and introducing this value of A into the equations of the first row, the result is

$$(\rho_i+i\omega m_i)a_i-i\frac{4\pi e_i}{D\omega}\sum_j\bar{n}_je_ja_j=\rho_ia_0 \tag{10}$$

representing z equations to determine the z values of $a_1, a_2, \cdots a_i \cdots$ as multiples of the value a_0 characteristic for the velocity of the solvent.

For all practical purposes it will be enough to give an approximate solution of these equations, keeping in mind that always ωm_i will be very small compared with ρ_i.

A zero order solution will be attained if we neglect ωm next to ρ altogether. Multiply every one of the Eqs. (10) with the corresponding product $\bar{n}_i\cdot e_i/\rho_i$ and take the sum of all the equations. The result will be

$$\sum_j\bar{n}_je_ja_j\left[1-i\frac{4\pi}{D\omega}\sum\frac{\bar{n}_ie_i^2}{\rho_i}\right]=a_0\sum n_ie_i=0,$$

[1] Diffusion is not considered; its effect is altogether negligible for our problem.

showing that in a zero order approximation $\Sigma_j \bar{n}_j e_j a_j = 0$, which according to (9) would mean $A = 0$ and therefore no potential differences at all. If they occur nevertheless we see that they will be exclusively due to the dynamical reactions of the ions measured by the products ωm_i. Now if as we found in the zero order approximation $A = 0$, and if ωm is neglected, the first row of (8) shows that in this approximation $a_i = a_0$. In a next *first* order approximation we will assume

$$a_i = a_0 + \beta_i \tag{11}$$

and treat β_i as a small quantity, neglecting products of β_i with the small quantities $\omega m_i/\rho_i$. Divide every equation of (10) by the corresponding value of ρ_i and keep in mind the rule of the first order approximation. Instead of the Eqs. (10) we will then arrive at the equations

$$\beta_i - i\frac{4\pi}{D\omega}\frac{e_i}{\rho_i}\sum_j n_j e_j \beta_j = -i\frac{\omega m_i}{\rho_i} a_0. \tag{12}$$

This set of equations enables us at once to calculate the value of $\Sigma \bar{n}_j e_j \beta_j$; we find

$$\sum \bar{n}_j e_j \beta_j [1 - i(4\pi/D\omega)\sum(\bar{n}_i e_i^2/\rho_i)] = -i\omega \sum(\bar{n}_j e_j m_j/\rho_j) a_0. \tag{13}$$

Now according to (9) and (11),

$$A = i(4\pi/D\omega)\sum \bar{n}_j e_j a_j = i(4\pi/D\omega)\sum \bar{n}_j e_j \beta_j. \tag{13a}$$

In this approximation we will have an electric field and the field strength will be determined by the expression for A, which results from the combination of (13) and (13a), namely

$$\frac{A}{a_0} = \frac{4\pi}{D}\frac{\sum(\bar{n}_j e_j m_j/p_j)}{1 - i(4\pi/D\omega)\sum(\bar{n}_j e_j^2/\rho_j)}. \tag{14}$$

The field strength X itself is according to (6) represented by

$$X = A e^{i(\omega t - kx)}.$$

IV.

To discuss the magnitude of the effect we go back to the potential Φ of which the field strength X can be deduced by the well-known equation $X = -\partial\Phi/\partial x$. For this potential, the expression

$$\Phi = g a_0 \frac{(4\pi/D\omega)\sum(\bar{n}_j e_j m_j/\rho_i)}{i + (4\pi/D\omega)\sum(\bar{n}_j e_j^2/\rho_j)} e^{i(\omega t - kx)} \tag{15}$$

is easily found starting with the value for A indicated in (14). So we get the result that a sound wave travelling with the velocity g and in which the velocity of the medium oscillates between $\pm a_0$ will be accompanied by a potential wave travelling with the same velocity and in which the potential will oscillate between the values of $\pm\Phi_0$, this amplitude being represented by the formula

$$\Phi_0 = g a_0 \frac{(4\pi/D\omega)\sum(\bar{n}_j e_j m_j/\rho_j)}{[1 + ((4\pi/D\omega)\sum(\bar{n}_j e_j^2/\rho_j))^2]^{1/2}}. \tag{16}$$

At the same time the material wave and the potential wave will show a phase difference which, however, we need not consider here.

We observe that the expression $\Sigma(\bar{n}_j e_j^2/\rho_j)$ is nothing else than the conductivity of the solution expressed in electrostatic units, which we will denote by l. Introducing this notation a more convenient form for Φ_0 will be

$$\Phi_0 = g a_0 \frac{\sum(\bar{n}_j e_j m_j/\rho_j)}{\sum(\bar{n}_j e_j^2/\rho_j)} \cdot \frac{4\pi l/D\omega}{[1 + (4\pi l/D\omega)^2]^{1/2}}. \tag{16a}$$

If now we have a solution of one salt containing $\bar{n}$ molecules per cc, of which every one is split in p_1, p_2, $\cdots$ p_i $\cdots$ different ions of valencies ζ_1, ζ_2 $\cdots$ ζ_j, we have $\bar{n}_j = p_j \bar{n}$; $e_j = \zeta_j \epsilon$, where ϵ is the electronic charge ($4.77\ 10^{-10}$ e.s.u.) and the valency ζ_j is taken with its appropriate sign; $m_j = M_j m_H$, if M_j is the molecular weight of the ion, together with the bound solvent molecules and m_H is the mass of the hydrogen atom $1.64 \cdot 10^{-24}$ g. Introducing these notations we find

$$\Phi_0 = \frac{m_H}{\epsilon} g a_0 \frac{\sum(p_j \zeta_j M_j/\rho_j)}{\sum(p_j \zeta_j^2/\rho_j)} \cdot \frac{4\pi l/D\omega}{[1 + (4\pi l/D\omega)^2]^{1/2}}. \tag{16b}$$

Now, if as an example we are dealing with a 10^{-3} normal solution of a binary salt like KCl or LiBr, etc., the order of magnitude of l will be $l = 10^9$ (if we assume $\rho = 2.10^{-9}$) and therefore assuming $D = 80$ the quotient $4\pi l/D\omega$ will become equal to 1 for $\omega = 10^8$ approximately. This frequency would roughly correspond to radio waves of 30 meters wave-length and would make the last part of the expression (16b) equal to $2^{-1/2}$. Using a lower frequency (for the special solution considered) would mean bringing the value of that part of the expression nearer to 1. The same thing would occur if the concentration is increased. That is

why in judging the magnitude of the effect we will take it that the expression $(4\pi l/D\omega)/[1+(4\pi l/D\omega)^2]^{1/2}$ can and has been made equal to 1. By adopting the usual values for m_H and ϵ and taking $g=1.4.10^5$ cm/sec., the first factor in (16b) becomes equal to $(m_H/\epsilon)ga_0=4.8\times10^{-10}a_0$. By using this factor the potential would be expressed in electrostatic units. Using volts instead, we find for the order of magnitude of Φ_0, the value

$$\Phi_0=1.4\times10^{-7}a_0\frac{\sum(p_i\zeta_iM_i/\rho_i)}{\sum(p_i\zeta_i^2/\rho_i)}\text{ volts.}\quad(17)$$

Now in our example, we would have $p_1=p_2=1$, $\zeta_1=+1$, $\zeta_2=-1$ and therefore instead of (17)

$$\Phi_0=1.4\times10^{-7}a_0\frac{M_1/\rho_1-M_2/\rho_2}{1/\rho_1+1/\rho_2}\text{ volts.}\quad(17a)$$

It is obvious that with $a_0=1$ cm/sec. and with appropriate salts, the oscillations of the potential should attain values of some 10^{-6} volts, which can easily be detected by ordinary amplification methods.

The question if $a_0=1$ cm/sec. is not too large a value to be assumed, remains to be answered. Now this velocity amplitude corresponds to a pressure-amplitude of 1/7 atmosphere and to an energy delivered per cm^2 and sec. of 1/200 Joule. It seems that this is not unreasonable at all thinking of a vibrating quartz-crystal, and that even more can be expected.

Experiments to detect the effect discussed here are being set up; no definite results are as yet available. As, however, the considerations put forward in this article seem to lead to an entirely new attack on the problem of solvation, I hope that I may be permitted to present them even in their present incomplete form in order to share in the congratulations at the birthday of this new journal.

The Chemical Bond

GILBERT N. LEWIS, *Department of Chemistry, University of California*

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IT was not long ago that the physical and the chemical pictures of the atom and the molecule seemed almost irreconcilable. Indeed, when the quantum theory was young, it could not be surmised that the development of that strange theory would bring about the reconciliation. Yet the chemist has always assumed, without being fully aware of it, a sort of quantum theory. The battle fought in the early years of chemistry between the theory of a continuous gradation between chemical substances, and the theory of discrete states, resulted in a complete victory for the latter theory. Thus, in the development of organic chemistry it became necessary to recognize that a molecule of given composition might occur in a certain limited number of isomeric states, and such a set of organic isomers now affords one of the best examples of a given system in several distinct quantum states.

Structural organic chemistry, although developed without mathematics, except of the most elementary sort, is one of the very greatest of scientific achievements. An enormous mass of information was reduced to a well-ordered system through the aid of a few simple principles. It was this system of structural chemistry that served chiefly as my basis when I advanced my theory of valence. The main feature of this theory was a set of simple *electronic* structures of such sort that if one asks whether a given molecule has a given electronic structure, the answer must be yes or no. The molecule may snap from one structure to another but there are no continuous gradations such as would be expected from classical electromagnetic theory. Such an electronic structure was pictured as capable of changing its form, or its energy, or its electric distribution, without changing its essential type.

Thus I visualized a sort of articulated skeletal structure in which the different parts have some freedom without change of articulation, but which is also capable of an abrupt change of articulation to produce a new structural type. Aside from the chemical behavior, this transition from one structural type to another was best evidenced by the magnetic susceptibility, for the change from a diamagnetic to a paramagnetic molecule is sudden and complete. More recently we have found other criteria of skeletal structure, especially in spectroscopy. Here we find differences in spectroscopic terms which could not conceivably be bridged by a continuum.

It seemed a little strange to attribute this essential skeletal structure to the electrons which have always been regarded, and are still regarded, as the most mobile part of a molecule. This view, however, is substantiated by modern spectroscopic analysis in which it has been found extremely useful to distinguish those vibrational and rotational levels which are due to the atoms from the levels which are due to the electrons, and it ordinarily requires far more energy to produce a transition from one electronic level to another, than it does to change the atomic level.

This idea of electronic structure, and, in fact, all the structural ideas which are used by chemists, were obtained by a method which may be called analytical, in the sense that from a large body of experimental material the chemist attempts to deduce a body of simple laws which are consistent with the known phenomena. The mathematical physicist, on the other hand, postulates laws governing the mutual behavior of particles and then attempts to synthesize an atom or a molecule. When the attempt is successful he has a weapon of extraordinary power which enables him to answer questions quantitatively which at best could be answered qualitatively by the other method. On the other hand, an inaccuracy in a single fundamental postulate may completely invalidate the synthesis, while the results of the analytical method can never be far wrong, resting as they do upon such numerous experimental supports.

It was a recognition of this fact, when I first deduced the idea of the electron pair bond from

an analysis of chemical facts, that emboldened me to accept this deduction; although it was obviously incompatible with the then accepted laws of electromagnetics and mechanics. The qualitative principles of molecular structure were presented, so to speak, as the minimum demands of the chemist which must eventually be met by the more far-reaching and quantitative work of the mathematical physicist. They have not been altered during the recent unprecedented period of discovery in mathematical and experimental physics; but it is now possible to amplify a little, and to express more nearly in the language of modern physics, these minimum demands, or qualitative specifications, to which we have reason to believe the quantitative results of mathematical physics must eventually conform.

I should have liked to show how, step by step, from the first investigations of Heisenberg and Schrödinger and Pauli, to the recent studies by Slater and by Pauling of the tetrahedral eigenfunctions, the physical picture has been brought successively nearer to meeting the qualitative chemical demands, and to point out some of the remaining gaps, but this I cannot do in any systematic way. There can be no question that in the Schrödinger equation we very nearly have the mathematical foundation for the solution of the whole problem of atomic and molecular structure, but there are two reasons why we cannot immediately deduce from this equation all the desired facts, and these two reasons are of very different character. In the first place, the equation is incomplete in that it ignores the phenomenon of spin, which is of such vital importance both to the chemist and to the spectroscopist. In the second place, even with a complete mathematical foundation, the intricacy of the problem usually prevents a satisfactory solution. When we remember the difficulty in Newtonian mechanics of solving the three body problem, and in relativistic mechanics even the two body problem, we see that the problem of the many bodies contained in the atom and the molecule cannot be completely solved without a great further development in mathematical technique. It is for this reason that the chemist and the spectroscopist must long be content with results that are qualitative, or only half quantitative.

The Structural Framework

There is one set of conclusions arrived at both by chemists and by spectroscopists, which, while seeming not inconsistent with quantum mechanics, can hardly be said to have been deduced from the mechanical equations. Both agree in assigning to the atom or molecule a certain pattern or framework. The chemist says that in proceeding from the hydrogen atom through the atoms of successively higher atomic numbers, electrons fall into the first shell, then into the second, and when these are both filled they fall into the third shell, but before this is completely filled they begin to enter the fourth shell, leaving certain positions in the third shell *unoccupied*. The spectroscopist says that there are certain quantum states which he names by analogy to the possible quantum states of the hydrogen atom, and these states may be occupied or unoccupied by electrons. In both cases a pattern is assumed which sometimes is supposed to have spatial significance like a set of pegs upon which hats might be hung, or sometimes it is considered to have purely ordinal significance like the numbered and lettered cards in a library catalogue, some of which might contain the names of books, while others might be left blank until the entering of new books. In either case we have a framework of positions some of which may be empty.

Now we are convinced that the specifications for the quantum state should be specifications for the atom or the molecule as a whole, but since the total number of specifications necessary to fix completely the quantum state of a system of N particles is $3N$ (ignoring spin for the moment), one is tempted to divide the whole set of specifications into N sets of three specifications each, and then to ascribe each set of three to one of the particles. This, however, is not permissible. Anyone who has studied the beautiful treatment of the two-electron problem given by Heisenberg must see the impossibility of saying anything of one electron which is not at the same time said of the other. We can, however, avoid this difficulty. For example, in the case of N electrons, we may set up our framework or cataloguing system with N series, each series consisting of sets of quantum specifications, three to a set. Then we

can say, not that a given electron is in one position or another, but only that N positions are occupied and the rest are unoccupied.

This is essentially the classification resulting from Bohr's theory of atomic structure, which gave a spatial significance to the various orbits that might or might not be occupied by electrons. Formerly, in discussing the Bohr theory of chemical structure I stated that we should "refer to the position of the orbit as a whole rather than to the position of the electron within the orbit." The Bohr orbit has now been replaced by its less tangible counterpart in quantum mechanics. We may still maintain the notion of certain spatialized loci and we may, I think, without danger of misunderstanding, still refer to these loci as orbits, using the word in a generalized sense. We thus visualize a set of orbits which may be occupied by not more than one electron at a time, but which may also remain unoccupied. I feel that it is a mistake to identify these orbits with the spatial distribution corresponding to a given eigenfunction of quantum mechanics, for the eigenfunction ordinarily refers to a distribution either in the $3N$-dimensional configuration space, or in some division of that space which cannot as a rule be identified with our physical space.

The orbits belonging to a single atom are ordinarily grouped according to the principle quantum number. Those having a principle quantum number of one are said to belong to the first, or K shell of the atom, those of principle quantum number two are said to be in the second shell, which may be divided into the s sub-shell and the p sub-shell. These two sub-shells together are equivalent to the octet. In the third and higher shells there is also the d sub-shell, which, however, is not often occupied by the valence electrons, so that the octet retains its significance even in elements of high atomic number. There are, however, numerous cases, especially among the so-called coordination compounds, in which Pauling has clarified a number of difficult questions by making use of d orbits merged with the s and p orbits, as the two latter are believed to merge in the formation of the octet.

Pairs and Bonds

In my original theory of valence, aside from the theory of the completed shells, which was advanced at the same time by Kossel, and which I shall presently have occasion to discuss more fully, the two most essential features were the electron pair and the chemical bond of shared electrons. Between these two phenomena there is no immediate connection. The pairing of electrons occurs in nearly all chemical substances, whether or not the pairs serve as bonds. Ten years ago I wrote, "there is nothing in the known laws of electric force, nor is there anything in the quantum theory of atomic structure, as far as it has yet been developed, to account for such pairing." This ceased to be true after the discovery of the remarkable principle of Pauli and of the phenomenon of electron spin. To our former quantum specifications we must add the new quantum specification of spin, so that in place of every one of our former orbits, each capable of being occupied by one electron, we now have a pair of orbits with opposite spins.

The change in energy of a system when one of its orbits becomes occupied depends largely upon what other orbits are already occupied. There is, however, a certain rough approximation to additivity of orbital energies which enables us to say, for example, that there is a wide difference of energy between the two $1s$ orbits and the two $2s$ orbits, that there is a considerable difference in energy between the two $2s$ orbits and the six $2p$ orbits, but that there is a small difference between the several $2p$ orbits. Therefore when electrons are successively added to the atomic nucleus the first electron enters a $1s$ orbit, the second enters the other $1s$ orbit, completing the pair and also the first shell. The next electron enters a $2s$ orbit, the fourth enters the second $2s$ orbit, completing the pair (and the sub-shell). Now we shall see that there is no "force" that draws two electrons into a pair. If we are to speak at all of a force between the two electrons of a pair, it is on the whole a repulsive force, for, as the electrons begin to enter the three pairs of p orbits, the first two do not enter the same pair of orbits, and they therefore do not form an electron pair. This is the state of affairs in the free carbon atom in its lowest energy state.

Numerous examples of this sort, when several pairs of orbits have nearly the same energy and the electrons consequently do not enter in pairs, have been found by spectroscopic research, and by the study of the magnetic properties of what I have called the transition elements.

There has been some tendency among physicists to speak of any two electrons as paired if they have opposite spins. This is far from my own idea. I think, rather, of a pair of occupied electronic orbits as fusing into a single entity, and claim that whenever it is permissible to assign separate quantum specifications to the several orbits, then the two orbits of a pair must be given the same four quantum specifications (for example n, l, m_l and m_s) except for sign. To the pair of electronic orbits we must unquestionably give opposite values of m_s and the same values of n and l. There may be some question regarding the other quantum number, m_l. Professor Latimer, to whom I am extremely grateful for many interesting discussions of the problems considered in this paper, suggests that if the two values of m_l are not zero, they should be taken to be opposite in sign. From this it would result that the electron pair would contribute neither spin-moment, nor angular momentum. As far as I am aware, there are no facts opposed to this view.

Not only is the pair of electrons not necessarily a bond, but the bond need not always be a pair. The simplest case of a molecule in which two atoms are held together by a single electron is the hydrogen molecule ion, H_2^+, first discovered by J. J. Thomson. One might perhaps expect to find many examples of the one electron bond among the enormous number of known chemical substances, but on the contrary, it is a very rare phenomenon, and it is doubtful if there is a single known case of a stable chemical substance in which there is good evidence for the one-electron bond. There is one thing that we can say pretty certainly from chemical, and especially from spectroscopic evidence, regarding the single electron bond, and in fact regarding unpaired electrons in general. If an atom or a molecule contains one or more unpaired electrons, or in other words, if any orbit is occupied when the other orbit of the pair is unoccupied, then either in its lowest state or in a state which will appear at moderate temperatures, the atom or molecule will exhibit paramagnetism. This is the most effective criterion for determining the existence of unpaired electrons.

In order to account for the structure of the hydrides of boron, which have too few electrons to assume the normal octet structure, Sidgwick proposed that two of the bonds between boron and hydrogen in B_2H_6 are single electron bonds. This idea has been amplified by Pauling through the assumption that it is no two particular bonds that permanently have this one-electron character, but rather that this character alternates among the several bonds in a sort of resonance. As far as I am aware, the magnetic properties of these substances have not been studied, but when they are, I shall be surprised if any paramagnetic behavior is observed. I shall propose presently another explanation of these structures which seems more probable.

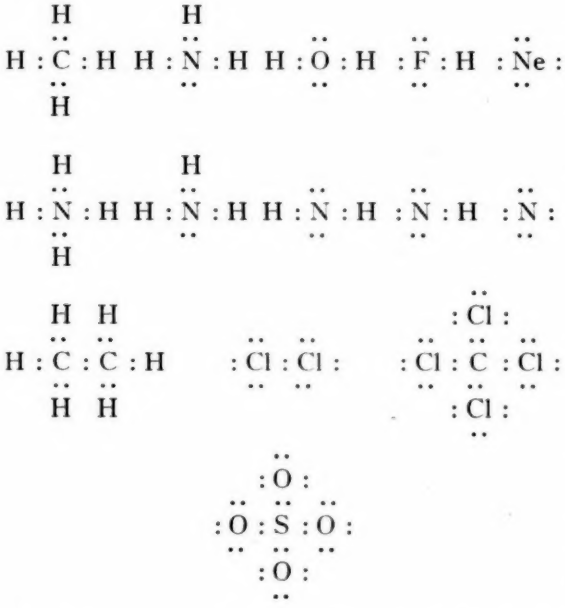
The reason for the scarcity of the one-electron bond is apparently two-fold. In the first place, most of our chemical substances have completely occupied shells or sub-shells, so that pairing is inevitable. In the second place it has been pointed out by Pauling that the single electron bond is not very stable, especially when two unlike atoms are thus bonded. On the other hand, the ordinary two-electron bond stabilizes the pair of electronic orbits which constitutes the bond. The work of Heitler and London made it possible to calculate the energy of some simple systems containing two electrons shared by two atoms. While their calculations were of the utmost importance as a step towards the quantitative study of such systems, I cannot admit that it threw any further light upon the phenomenon of pairing, since their method of calculation could be applied to any two electrons in any two quantum states, or even to a system of two atoms and three electrons.

Unlike the one-electron bond, the three-electron bond, which has sometimes been proposed, is, to my mind, unthinkable. We could, however, have a three-electron double bond with two occupied orbits in one bond, and one in the other. (So also we might have double bonds with only two unpaired electrons.) But all such molecules would exhibit the paramagnetic behavior to which I have referred, and I know of no case where there seems to be any reason to believe in

their existence, except possibly in such an ion as that of ethylene from which one electron has been removed.

The Steric Implications of the Octet

We now come to a discussion of those simple electronic structures which are so important to chemists, and in which the valence shell of each atom is fully occupied, or in other words, is a completed shell. Let us write down some of the simple electronic structures with which we have to deal.

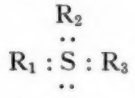


The first two rows illustrate the case of the single octet with or without protons bonded by the electron pairs. The remainder represent cases in which two octets share a pair of electrons, the bonding pair. We shall say that the dots represent, not individual electrons, but occupied electronic orbits.

One of the facts which chemists have been at greatest pains to establish is the fact of the perfect symmetry of the methane molecule. When, however, the present system of spectroscopic classification was introduced, this fact was doubted because the eight electrons of the valence shell of carbon were classified as two *s*-electrons and six *p*-electrons. It is now generally recognized that the two views may be reconciled by a sort of merger of the *s*-orbits and the *p*-orbits in such manner as to give four equivalent pairs of orbits. Pauling effects such a merger by an expedient which, unfortunately, breaks the continuity of electronic structure between the methane molecule and the neon atom. The equivalence of these two electronic structures is a point which I insisted upon strongly in my first paper, and upon which I still think that I must insist. When we consider the series of structures from methane through ammonia, water, hydrogen fluoride, to neon, or still better, if we consider the next series obtained by successive removals of one proton from ammonium ion to give ammonia, amide ion, imide ion, and nitride ion, we see how arbitrary it would be to assume a discontinuity of electronic structure about the central atom in such series.

Now the chemist requires not only the equivalence of the four hydrogens in methane, but also a spatial, or steric, arrangement of these atoms. He requires a tetrahedral arrangement about the carbon atom,—a regular tetrahedron if the four entities attached to the central atom are the same, as in methane and carbon tetrachloride, and an irregular tetrahedron if any two of these entities are different. When all four of the entities are different he measures the asymmetry of a molecule by its optical rotatory power.

When one of the protons belonging to ammonium ion is removed, while the electron pair which served as bond remains in the molecule, does this non-bonding pair sink into an *s*-shell, leaving the six *p*-orbits to rearrange themselves in a triangular, or two-dimensional arrangement, as distinguished from the three-dimensional, or tetrahedral arrangement? The answer is decidedly in the negative. The non-bonding pair remains as one of the entities which determines the tetrahedral character of the molecule! It is true that when the three hydrogens of ammonia are replaced by three dissimilar groups, it has not yet been possible to resolve the two optical isomers. Nevertheless, the tetrahedral form about the nitrogen atom is the accepted explanation of the isomerism of the oximes, and in the quite similar structures of the sulphonium type,



numerous substances have been resolved into their optical isomers.

When we come to the next type, represented by water and imide ion, we can no longer hope to find the phenomenon of optical rotation, since two of the entities attached to the central atom are now alike, namely, the two non-bonding pairs; but their steric effect is still manifest in the departure of the molecule from a linear form. I realize that attempts have been made, both by chemists and by physicists, to show that two bonds might, in their normal state, assume an angle less than 180°, even in the absence of other bonds or pairs, but I have never seen any evidence, theoretical or experimental, that seems to warrant such a conclusion. On the contrary, I believe that whenever we have four electron pairs on the central atom, we have a tetrahedron, regular or irregular; that when we have three pairs we have a triangle, while two pairs give a linear structure. Thus in the case of such ions as CO_3^{--} and NO_3^-, in each of which, according to the structure first proposed by Latimer and Rodebush and since abundantly corroborated, there are only three electron pairs binding the three oxygens to the central atom, a structure in three-dimensions was at first suspected, but it is now agreed that the form of each is an equilateral triangle with the carbon or nitrogen atom centrally placed.

When we come to molecules such as HF and NH^{--}, we no longer have any means of determining the steric effect of the non-bonding electron pairs, but it seems hard to believe that the presence of one more non-bonding pair has produced a change in the essential structure of the molecule. Finally, by removing one more proton from the imide ion, we are left with the neon structure. There will be many who will grant the tetrahedral structure of methane, or even of ammonia, but who will be strongly averse to assigning any such structure to neon. Thus the student of quantum mechanics will show that in neon, with its completed shells, the electron cloud is distributed with perfect radial symmetry. But this, in fact, could also be shown to be true of the methane molecule. The distribution given by quantum mechanics is an average distribution over infinite time, and such a distribution, calculated for methane, would show a central nucleus with spherical shells of negative electricity, and, mainly outside of these, a spherical shell of protons. This is simply because the tetrahedral atom would, in course of time, pass through all orientations, so that in the statistical average no directions would be unique.

If, instead of methane, we consider carbon tetraiodide, the same thing would be true, but owing to the large mass of the iodine atoms, the system would be more sluggish, and it would be less useful to speak of the spherical distribution of the atoms. We might compare carbon tetraiodide, methane, and neon, with the hour hand, the minute hand, and the second hand of a watch, a photograph of each of which, taken over a day, would show a uniform disk, but this would not be true for short exposures.

On account of the complexity of quantum mechanics in the problem of many bodies, it frequently happens that two investigators, basing their work upon this mechanics, are led to widely different physical views of the atom or molecule, but this is ordinarily because they are dealing with different first approximations, both of which are far removed from ultimate reality. On the other hand, even when an accurate solution of the Schrödinger equation is obtained, it is usually a special, and not a general solution, so that there may be another apparently quite different solution which is equally satisfactory. It is quite possible, if the average electric distribution about the neon kernel were accurately obtained by means of the Schrödinger equation, that we should find indications of two concentric, but largely overlapping shells, one of which might be called the *s*-shell, and the other the *p*-shell, but I see no reason for believing that two-electron orbits would be confined chiefly to the former and six to the latter. The same distribution might equally well be attained by four equivalent pairs of electron orbits. Nor do I see that there is anything in quantum mechanics to prohibit a schedule for the electrons upon their several tracks, or to put it less figuratively, phase relations within the several orbits, such as would give to the neon atom the pattern of a regular tetrahedron.

After all, however, I wish to lay no stress upon the tetrahedral character of the neon atom, and it is of no practical utility. There is no ques-

tion but that the tetrahedral character becomes greatly enhanced, and also becomes more important scientifically, when atoms are bonded by the four-electron pairs. I have only entered upon this discussion because I wish strongly to reaffirm my belief that the fundamental electronic structure, with respect to the central atom, is the same from methane to neon, inclusive, and that the tetrahedral character of methane is not caused by a promotion to a different quantum state from that represented by neon.

The Molecule with Completed Electronic Shells

In the study of atomic spectra there is peculiar significance to the completion of an electronic shell, or even of a sub-shell. The atom of neon has its first and second shells completely occupied. It has no uncompensated electronic spins, no angular momentum, no magnetic moment, and no electric moment. It is a singlet state indicated by spectroscopists as ^1S. If now we consider that the electrons of a bonding pair help to fill the shells of both the bonded atoms, then we may say that in the molecule of methane the carbon is in a similar state to that of neon, while each hydrogen has its completed first shell. This molecule also has no resultant spin, no angular momentum, and no magnetic moment (but it may have an electric moment when the hydrogens are replaced by different groups). Since spectroscopists have decided to distinguish between atomic and molecular types, methane is said to be in a singlet state, known as the $^1\Sigma$. This is not true only of methane, it is probably true of all molecules that chemists call saturated.

Some spectroscopists, in discussing molecular states, have started with what seems to be a mistaken extension of the Pauli principle, and therefore have been led to the very unpromising idea that a molecule can have only two electrons in its first, or K, shell. It seems to me almost self-evident that when two chlorine atoms combine, the two K electrons of each atom are almost undisturbed. If this is admitted, we are led to consider the valence electrons also, or rather, the occupied electronic orbits, as belonging to the shells of individual atoms, and when this is done we have, at least in the case where all shells are completely occupied, just the picture of electronic structure that I have presented.

In a molecule consisting of atoms A, B, and C, the several electronic orbits may be designated as A-orbits, B-orbits, and C-orbits, except that certain pairs of orbits should be designated as AB-orbits, or BC-orbits, if there is a bond between A and B, and between B and C.

Thus in the molecule $:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\text{Cl}}}:\text{Br}:$ we may say that there are three pairs of non-bonding Cl-electrons, three pairs of non-bonding Br-electrons, and also one pair of bonding ClBr-electrons. If now we are discussing another molecule $:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\text{Cl}}}:\text{I}:$ with the same electronic structure, we must consistently bear in mind that there are large differences possible within this same structure, so that these two molecules may differ greatly in energy, in the distance apart of the atoms, and in electric moment, but these are differences within the same articulated structure and represent no change in articulation.

It is to be noted that when we assign the several occupied orbits to the individual atoms, or to pairs of bonded atoms, it makes no difference whether these atoms are unlike or identical, for we must remember that when the rotational and vibrational quantum numbers of the molecule are fixed, every atom in the molecule is thereby distinguished from every other atom, even though some of the atoms be identical.

In discussing a bond we must avoid saying that one electron of the bond comes from one atom and that the other comes from the other atom. We are not interested in the history of the particles that enter into our system. It is often of value in approximate applications of our mathematical methods to consider a hydrogen ion and a chloride ion coming from an infinite distance to form the molecule HCl, or again to consider a hydrogen atom and a chlorine atom uniting to form the same molecule. In the first case the chloride ion might be said to have furnished both electrons of the bond, while in the second case one would be said to come from the hydrogen atom and one from the chlorine atom. In both cases the same bond is produced, and in that bond the two occupied electronic orbits

must be regarded as welded into a single entity.

If we ignore spin, any non-bonding pair requires three quantum specifications in addition to the designation of the atom to which it is attached. Now it is also true that a bonding pair is fully described when we state which two atoms it binds, together with three, and never more than three, further quantum specifications. This is a point of so much significance that it requires some amplification. Let us consider the simplest of all bonded systems, the hydrogen molecule ion. Here we have a system of two protons and one electron. Making use of the universal rule that each particle contributes three degrees of freedom to the system (again ignoring all spins), we have a total of nine degrees of freedom. This is another way of saying that the quantum state of the system can be fully described by nine quantum specifications. Three of these degrees of freedom are assigned to the translation of the molecule as a whole, two to rotation of the molecule, and one to its vibration. This leaves only three degrees of freedom for the representation of the electronic states, which is the same number that we would have for an electron attached to a single atom.

It would therefore seem, on hasty inspection, as though it would be incorrect to say that a bonding pair has one principal quantum number with respect to one atom and another with respect to the other, but this conclusion is not valid. The principal quantum number of an electron with respect to either atom is associated with the average distance from electron to atom. Likewise the vibrational quantum number is associated with the distance between the two atoms. Now if two of these distances are given, the third is determined. We shall, therefore, find it useful to speak of the principle quantum number of a bonding pair with respect to each of the atoms to which it is attached. So in methane we have assumed that each electron pair is in the second shell of carbon and the first shell of hydrogen; and this is presumably true of every bond between carbon and hydrogen.

In speaking of the electronic structure in the series CH_4 to HF, I stated that this was the same electronic structure with respect to the central atom. It seems not to be the same with respect to the hydrogen atom. While methane is the type of a saturated molecule; water, ammonia, and hydrofluoric acid behave very differently. Their strong tendency to form complex molecules cannot, I believe, be explained except by assuming the hydrogen bond of Latimer and Rodebush. According to this assumption a hydrogen atom may be bonded to two other atoms. Now it would be impossible for both the two bonded pairs to be in the first shell of hydrogen. We must assume, therefore, that in these substances and probably in all others from which hydrogen can be easily removed as hydrogen ion, the bonding pair is not in the first shell of the hydrogen. This is essentially the view that I put forward in my book on Valence, where I wrote, "Hydrogen when attached firmly to a pair of electrons, as in the hydrogen-hydrogen or hydrogen-carbon bond, shows no tendency whatsoever to become bivalent, or in other words, to form a hydrogen bond. On the other hand, when combined with an extremely negative element like nitrogen, oxygen or fluorine, toward which the electron pairs are very tightly drawn, the bonding pair may be drawn out of the first valence shell of hydrogen into a secondary shell, and it is apparently under some such circumstances that the hydrogen atom can form a loose attachment to another pair of electrons, thus forming the hydrogen bond."

When a molecule like HF is excited to higher vibrational states, it is probable that in most of the new quantum states the bonding pair changes to higher principle quantum states with respect to the proton, until finally the molecule is broken into fluoride ion and hydrogen ion. Up to this point the bond exists, and to call it a "polar bond" at one stage or another of this process seems to contribute nothing to the subject. When I originally proposed the new theory of valence one of my chief hopes was that it might lead toward a simpler and more consistent nomenclature. It is with some sense of discouragement that I have seen the modern terminology developing. We have polar bonds and non-polar bonds, heteropolar and homopolar bonds, covalence bonds and semipolar double bonds.

No one who has accepted the electronic structure as the primary basis of chemical classification can possibly need these various kinds of bonds. Let us consider a molecule such as hy-

droxylamine which has the primary structure $:\ddot{N}:\ddot{O}:$, with three protons attached to three of the electron pairs. They are loosely attached in the sense that even in the lowest energy state of the molecule the bonding pairs are presumably not in the first principle quantum state with respect to the protons. These protons move about from one electron pair to another with the greatest ease. Now if two of the protons are attached to nitrogen and one to oxygen, then the bond between nitrogen and oxygen is called a "covalent bond," if all three protons are attached to nitrogen, then the bond between nitrogen and oxygen is called a "semipolar double bond," but if in a case like this we cannot assume a permanence of the electronic structure with respect to nitrogen and oxygen, then we might as well abandon our system altogether. The bond between nitrogen and oxygen is the same wherever the protons are, or even if some of them leave altogether as ions.

It is true that there are other things to talk about in the molecule besides the electronic structure. Thus it is useful at times to speak of the *formal* electric charge on each atom, which is obtained by subtracting from the number of positive charges on the kernel, the number of non-bonding electrons and half the number of bonding electrons which are attached to that kernel. This procedure will usually enable us to predict whether or not a molecule has a high dipole moment. However, all such properties are to be ascribed to the molecule as a whole, and not to some one bond in the molecule.

Whenever we have a free molecule, as in the gaseous state, I see no evidence for the existence of any other kind of bond than the one which we have been discussing under the name of the chemical bond. It is true that in the vapor of sodium chloride this bond may be easily broken. When chloride ion combines with sodium ion the pair of bonding electrons must start a new incomplete shell in the sodium atom. Moreover, this pair may possibly not be in the third principal quantum state with respect to the sodium, even in the state of lowest energy. If the molecule is activated, certainly some, and probably the most important, of the quantum states are those in which the bonding pair has a high principal quantum number with respect to the sodium. However, the bond persists until the molecule finally dissociates, and then there is no longer a bond.

Molecules with Incomplete Shells

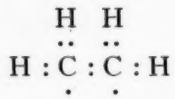
The molecules with completed shells are of extraordinary interest because of the simplicity with which they can be catalogued, and because the normal states of an enormous number of chemical substances are of this type. When we are considering the physical properties of saturated substances at ordinary temperatures, it is the electronic structure of completed shells that must be our guide. On the other hand, it is the excited states of the molecule which are of interest to the spectroscopist. These excited states must in the future be of equal interest to the chemist, because it is ordinarily through the intervention of such states that a chemical reaction occurs. However, the study of molecules with incomplete shells presents enormous difficulties and many of the rules which we have laid down for the saturated molecule can be used only as rough guides in an approach to an understanding of the unsaturated molecule.

Let us examine for a moment the organic chemist's use of the term "saturated." The hexamethylene molecule, C_6H_{12}, is called a saturated molecule, and is one in every respect, although if the ring were broken, it would not have enough electrons to fill all the valence shells. Now it was pointed out by Baeyer that as the number of methylene groups in the ring diminishes, there is an increasing strain, or instability, which becomes very evident in the trimethylene ring. According to Baeyer's theory, the series does not end with trimethylene, but with the two-membered ring ethylene, C_2H_4, only here the ring has become the double bond. Now in spite of this theory of Baeyer the organic chemist classifies this single member of the series, the ethylene molecule, as an unsaturated hydrocarbon. Here again his uncanny instinct proves to be sound.

We must not call a molecule unsaturated merely because it takes only a small amount of energy to change it to a new electronic structure. This, however, is true of the double bonds and we could arrange them more or less in the order

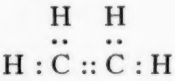
of increasing instability, C=C, C=N, C=O, N=N, N=O, O=O. In the case of molecular oxygen, one of the two bonds is definitely broken in the state of lowest energy. The unpaired electrons give rise to the pronounced paramagnetism of oxygen, and it is only among the excited states of oxygen that the spectroscopists have found the $^1\Sigma$ state in which we recognize the true double bond. So also the bond between nitrogen and oxygen in some nitroso compounds is broken, although we do not know in how many cases this is true. In the other cases, as far as is now known, the doubly bonded formula with completed shells represents the normal state of the molecule.

The mere fact that ethylene is near the breaking point would not justify us in calling it a truly unsaturated molecule. This is justified by another line of reasoning which indicates the difficulty of assigning definite formulae to unsaturated molecules. We have pointed out that it would not take much energy to break one of the ethylene bonds and thus produce a molecule of the oxygen type represented by



(a)

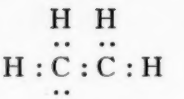
Now there is no way of compromising between this state and the normal state



(b)

One changes to the other in an abrupt transition which changes the whole character of the molecule. If we think of electronic orbits as tracks upon which the electrons can run, then we might say that in this transition the gauge of all these tracks is suddenly changed so that it would be impossible for an electron to run on both types of tracks simultaneously. On the other hand, there may be different formulae which represent the same essential electronic structure and these we must now examine.

We have said that a completed electronic structure will always give rise to a $^1\Sigma$ state of the molecule. The converse of this is by no means true. Thus if we should write for ethylene the formula

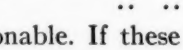


(c)

this also would presumably belong to the $^1\Sigma$ type and therefore would presumably be, if we may so speak, of the same gauge as the doubly bonded formula (b). Now if we have two formulae such as (b) and (c) which differ only in electronic arrangement and are of the same spectral type, or, as we have said, of the same gauge, then these two formulae cannot be regarded as two possible separate states of the molecule. They must rather be regarded as two different *representations* of a single structural state, which ordinarily has a lower energy than would be predicted if we should assume that there are two separate states and that some of the molecules are in one state and some in the other.

This is the phenomenon which has been called by Ingold the T-effect and which has been studied recently by Pauling under the name of resonance. We must not think that this phenomenon is due to the fact that we can write two or more different formulae to represent the same structure, but rather we must think that we can write two or more formulae because there has been a considerable loosening, without fracture, of the skeletal structure, so that within this skeletal structure there is far more freedom from the effects of quantum restrictions than in a saturated molecule such as ethane.

In the case of ethylene, formula (c), which is one of the ways of representing the compromise or resonance state, shows a structure of incompleted shells, and it is for this reason that we are justified in speaking of ethylene as an unsaturated molecule. On the other hand, in this particular case formula (c) represents an extreme displacement of electric charge from one side of the molecule to the other and presumably, therefore, plays only a minor part in determining the properties of the compromise state. This is no longer true in acetylene where the formulae H : C ::: C : H (a) and H : C : C : H (b) might



seem equally reasonable. If these are two ways of expressing the same fundamental electronic structure, the properties of the system may perhaps be more nearly represented on the basis of the second rather than the first of the two. On

the other hand, if formula (b) represented the only possible form of the molecule, it would presumably not be stable, for by analogy to the results obtained from atomic spectra, we should expect this form alone to be unstable with respect to H : C : C : H (c) which would represent an entirely different type of electronic structure. However, the compromise state, of which formulae (a) and (b) may be regarded as two reasonable representations, is stable with respect to any other different type of electronic structure such as is represented by formula (c).

It seems to be a rule that when two electrons are absent from a completed shell, the two empty orbits will not belong to the same pair, unless all the electrons present are employed in forming bonds, in which case the pairs are stabilized by acting as bonds. Thus there is a sharp contrast between the oxygen atom with its six electrons, two of which are unpaired, and the nitrate and carbonate ions in which there are six electrons on the central atom, which, however, are all employed in forming the bonds with oxygen. These ions therefore behave as though they were, and almost undoubtedly will be found to be, in the $^1\Sigma$ state.

I wish now to raise a question concerning the meaning of the dots in the formulae that we have been using. In the ordinary case of the saturated molecule we have said that these dots indicate occupied electronic orbits. Therefore, by counting the dots, we have the total number of valence electrons in the molecule. Now, however, that we are discussing incomplete shells, shall we adhere to this rule, or shall we let the dots represent orbits which are occupied, as one might say, a considerable part of the time? I am inclined to suggest the latter, and to write for the hydride of boron, B_2H_6, the same formula that we have written for ethane, indicating in some way that two electrons are missing, so that on the average each bonding pair of orbits is occupied only six sevenths of the time. We shall then have a picture of a molecule in which all the electrons remain paired, but in which the orbits are not fully occupied. If we imagine the electrons in rapid motion throughout the several orbits, and in such phase relations as to preserve the pairs at all times, we should presumably diminish the strength of the bonds without altogether destroying their stability. In fact, we know that the boron-boron bond is broken when the hydrogens are replaced by other radicals. If B_2H_6 proves as I suspect that it will, to be in the $^1\Sigma$ state, I think that this will be the best way to represent its structure.

When a molecule of completed shells becomes unsaturated, it may do so through a change which renders some of its existing shells incomplete, or by beginning new shells. Thus in a paraffin hydrocarbon the only way in which electrons can be added is through the occupation of orbits which are higher than the first shell for hydrogen, or than the second shell for carbon. Phenomena of this sort undoubtedly exist. Triphenylmethyl seems to form a compound with hexane. There is no possible way of explaining the interesting phenomenon known as the Walden inversion without assuming that for a brief moment, at least, the asymmetric carbon atom has become quinquivalent. In this case it is probable, however, that the fifth atom does not attach itself unless one of the other four atoms is already (either in the normal state or through excitation) in a high principle quantum state with respect to its bonding pair.

Whenever we have one more or one less electron than the number required to fill the shells, in some cases it may be easy to locate the particular atom on which the excess or deficiency occurs. In other cases, however, we may only indicate the group of atoms where this occurs, and in extreme cases it may only be possible to say that the molecule as a whole has an excess, or a deficiency, of one electron. Even in my first discussion of the problem of odd molecules of the inorganic type, I took pains not to indicate which atom possessed the odd electron. In such extreme cases the usefulness of structural formulae may nearly disappear, but this is no reason why in other cases we should not use the structural formulae as far as they will go.

In the study of atomic spectra an extraordinary similarity has been found between states which have an electron in excess of the completed shell, and those in which one electron is lacking. The only suggestion that I feel competent to

make regarding molecular spectra is that we should start, as a norm, with the molecule of completed shells, assigning each electron orbit to a given atom, or to a given bond between two atoms. From the norm we should proceed, symmetrically in both directions, to the discussion of cases where one electron is in excess or one electron is lacking, proceeding next to the case where two electrons are in excess, or two are lacking. An attempt should be made to assign these electron excesses or deficiencies to individual atoms, although we know in advance that in some cases this attempt will fail.

I am afraid I have not contributed much to this difficult subject of the incomplete shells, but I believe that the study of such systems is the greatest field for the future development of chemistry and spectroscopy alike.

An X-Ray Study of the Wüstite (FeO) Solid Solutions

ERIC R. JETTE AND FRANK FOOTE, *School of Mines, Columbia University*

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A series of iron oxides with compositions between 76.08 and 76.72 percent Fe, all of them lying within the single phase solid solution area known as Wüstite has been prepared and the lattice constants and densities of the individual members determined. The NaCl structure found by earlier investigators and considered by them to be the structure of FeO has been found throughout this series. Contrary to the earlier results the size of the unit cell decreases as the iron content decreases. The solid solution is of a complex type; an oxygen ion replaces an FeO group with an accompanying increase in valence of 2 Fe^{++} to 2 Fe^{+++}. The results are discussed from the chemical and structural points of view.

INTRODUCTION

IN the binary system iron-oxygen there is a single phase solid solution area situated in the vicinity of the compound FeO. This phase is known, especially among the German metallurgists, as "Wüstite." Phase diagrams of the iron-oxygen system which include this area have been made on the basis of thermal analysis and microscopic examination by Pfeil,[1] Schenck and Hengler,[2] and Mathewson, Spire and Milligan,[3] to mention only three of the latest reports. In spite of much experimental work, it is still uncertain whether the Wüstite area actually includes the composition theoretically corresponding to FeO, reaches this composition as a limit at high temperatures, or has at all temperatures a minimum oxygen content significantly higher than the compound FeO. It may safely be inferred, that if either of the first two possibilities is correct, the minimum temperature will be above 1300°. The primary object in the present investigation was not to decide such questions but rather to study the crystal structure of the oxides lying entirely within this region. When it is recognized that from the chemical standpoint the oxygen content of such an oxide cannot be increased without at the same time changing the valence of its metallic constituent and further, that change of valence almost invariably involves a change of ionic size, such a series of single phase compositions as is possible within the Wüstite area is likely to involve solid solution phenomena of an unusual type. On account of the restricted scope of the present report and also because another investigation is in progress to determine, if possible, the limits of this area at various temperatures by x-ray methods, no attempt will be made here to discuss the relative merits of the several thermal diagrams which have been proposed.

PREVIOUS X-RAY INVESTIGATIONS

Two x-ray investigations have appeared dealing with compositions within the range of the present work, namely, by Wyckoff and Crittenden[4] and by Groebler.[5]

Wyckoff and Crittenden prepared the oxide by burning Armco iron in oxygen, resulting in a composition approximating Fe_3O_4, mixing four parts by weight of this with one part of iron and melting in an electric fusion pot. The resulting substance was ground up and remelted and the authors considered it to be a preparation saturated with iron. No other heat treatments are recorded. One of these preparations was subjected to magnetic purification and the final result was an oxide (No. 958 pur.) which analyzed 76.18 percent total iron and was considered as essentially ferrous oxide. Another oxide (No. 928) which ap-

[1] Pfeil, J. Iron and Steel Inst. (London) **123**, 237 (1931).

[2] Schenck and Hengler, Archiv. f. Eisenhüttenwesen **5**, 209 (1931).

[3] Mathewson, Spire and Milligan, Am. Soc. Steel Treat. **19**, 66 (1931).

[4] Wyckoff and Crittenden, J. Am. Chem. Soc. **47**, 2876 (1925); also Z. Krist. **63**, 144 (1926).

[5] Groebler, Physik. **48**, 567 (1928); this work is also reported with more detail as to preparation of the oxides in an article by Groebler and Oberhoffer, Stahl u. Eisen **47**, 1984 (1927).

parently had not been magnetically purified gave 75.24 percent total iron. It is quite evident from the complete analyses which the authors give, that No. 928 was not in a state of equilibrium and from a comparison with the results reported in the present work this is probably also the case with No. 958 pur. As the lattice constants, they found for No. 958 pur. that $a_0 = 4.29_4$A and for No. 928, $a_0 = 4.31_0$A, the latter showing many lines from Fe_3O_4.

They conclude: "The length of the edge of the unit cube of the ferrous oxide structure in No. 928 is consistently higher than a_0 for this substance in No. 958 pur. The existing measurements do not conclusively show that this difference in a_0 of 0.3–0.4 percent is outside the limit of experimental error because only three ferrous oxide lines could be measured in these photographs. These data, nevertheless, make it highly probable that this substance formed in the presence of much magnetite has a slightly larger unit cell than pure ferrous oxide."

Groebler prepared the entire series of oxides between Fe_3O_4 and Fe by the reduction of Fe_2O_3 in various mixtures of CO and CO_2 at 800°C. Of importance in the present connection is that for five preparations with total iron contents between 75.95 percent and 77.10 percent, his x-ray examination showed only the ferrous oxide lines but without any change in the position of these lines. The failure to observe any shift in these lines would indicate that the lattice dimensions remained constant throughout the range of solid solution. Groebler, however, reported no quantitative values for the lattice constants and merely gave a diagrammatic survey of the observed diffraction lines.

The results of the present investigation show that as the iron content of the oxides in the Wüstite area decreases there is an accompanying decrease in the lattice dimensions. They disagree, therefore, with the results of both the previous investigations.

Preparation of Materials

The preparation of iron oxides with compositions in the Wüstite area is very troublesome, caused chiefly by the fact that no suitable substance exists which will hold the materials involved at the required high temperatures. Any metallic container will react with iron; any nonmetallic refractory reacts with the oxide. Pure iron crucibles will serve for the iron saturated side of the series but not for the magnetite side nor the intermediate ranges. Platinum removes iron from the oxides, especially above 1100°C but even at 950°, after prolonged contact with the oxides in vacuo, there is an appreciable action. According to the thermal diagrams of the system the difference in iron content of the two limits of the solid solution at 1000° at the maximum is only about 2 percent. For the x-ray examination it is therefore necessary to have a series of oxides only a few tenths of one percent apart in composition while at the same time the individual samples should be chemically homogeneous, without physical strains due to grinding, etc., and of as high a degree of purity as possible.

The scheme finally adopted was to prepare large quantities of oxides with oxygen contents higher than desired, grind this material to 200 mesh, and mix with pure iron powder to secure the required composition. The thoroughly mixed material was wrapped in thin platinum foil, placed in an evacuated quartz tube and allowed to sinter at approximately 1050° for 24 hours. The tube was then rapidly cooled in water.

The large quantities of oxides were prepared by two methods. The first is analogous to that used by Pfeil.[1] Lumps of electrolytic iron were placed in an Armco iron shell supported on an aluminum boat. The whole was heated in air for two days at about 1050°C. The portion in contact with the iron shell was discarded. The interior of the lumps consisted of unoxidized iron. Two oxide specimens thus prepared analyzed 0.053 percent SiO_2 and approximately 74.3 percent Fe. This was used in preparing oxides Nos. 1, 3, and 4.

The second method consisted of heating pure Fe_2O_3 prepared from the oxalate and tightly packed in a covered heavy walled crucible of Armco iron in a high-frequency furnace. The temperature was increased slowly until the oxide skin which formed on the outside of the crucible melted and ran down the sides. Different compositions could be secured by varying the rate of heating, the temperature and the time at the high temperature but the composition could not

be controlled in any satisfactory way. Hence a number of melts were made in this manner, analyzed and the desired compositions selected. One having 74.24 percent Fe and 0.030 percent SiO_2 was used in making oxide No. 6; another analyzing 76.15 percent Fe and 0.018 percent SiO_2 was used for No. 7 and 8.

The iron powder was made by heating pure Fe_2O_3 (from oxalate) in an alundum boat first in air to remove undecomposed oxalate, etc., and then in a stream of hydrogen at 658°C until reduction was complete. This iron analyzed 0.015 percent Si.

When the mixture of oxides and iron powder were sintered at 1050° as mentioned above, the product was a firm rod of material which was then ground up and analyzed. The platinum foil was generally quite brittle after this treatment indicating that it had taken up some iron. It was seldom that satisfactory films were obtained from these oxides without further annealing treatment of 1 to 5 hours. This was also performed in platinum foil but generally at lower temperatures, which as far as possible were selected below the point where sintering becomes troublesome. At the limiting compositions of the series, however, temperatures above 900° were required to ensure that the substance was kept within the Wüstite area. The proper conditions were determined by a large number of preliminary experiments. The iron content was determined after each annealing.

In spite of all efforts, however, x-ray examination revealed that complete chemical homogeneity had not been attained in any of the samples. The change of lattice dimensions with composition within this range is quite considerable so that the x-ray photograms give a very sensitive test on this point. A difference of 0.10 percent Fe causes a shift of 0.6 mm in the position of the outermost reflections which corresponds to a change of 0.003A in the lattice constant. For chemically homogeneous substances no difficulty is ordinarily experienced in determining the positions of these outermost reflections to within ±0.2 mm and generally the measurements may be checked to within ±0.1 mm. With the iron oxides, especially at the high iron end of the series, distinct sharp spots indicating particles of different compositions would sometimes be spread over 2 mm. Such results were discarded and the samples given further annealing treatments until the lines were more uniform and narrow. Even so the total range of composition on the high iron side was probably of the order of ±0.07 percent Fe, which is of the same order of accuracy as the chemical analysis; this difficulty, while entirely absent in only a few cases, was much less for oxides at the magnetite end or at intermediate compositions.

Attempts were also made to prepare pure FeO by decomposition of FeC_2O_4 under conditions closely similar to those described by Andrew, Maddocks and Howat.[6] Decomposition in vacuo at 680–700°C always resulted in a product which gave a distinct iron pattern on the x-ray photograms. Even after prolonged annealing under these conditions the iron lines appeared although samples were obtained which analyzed 77.69 percent Fe (FeO=77.73 percent Fe). While our method was perhaps not absolutely the same as that of the above writers, our experience with it and the results of our x-ray analyses reported below give us no confidence that a substance analyzing 77.73 percent Fe and at the same time showing only lines from the NaCl type of structure can be prepared by such means. We have every reason to believe that if FeO as such exists at all it must be unstable at 700°C. An oxide containing 77.4 percent Fe annealed at 600°, 795°, 913° and 1035°C gave in each case iron lines on the x-ray photograms.

$FeCO_3$ precipitated, washed, dried and ignited without at any time coming into contact with air and with the ignition carried out in vacuo invariably gave nothing but magnetite.

Analytical Methods

The total iron content was determined by titration with $K_2Cr_2O_7$ by using such concentration that approximately 80 cc of solution were required for a 0.3 g sample. The titrations were carried out with the utmost care with frequent standardizations of the solution as a check on the technique. As standards, Fe_2O_3 prepared by the decomposition of pure ferric nitrate, Fe_2O_3 from Kahlbaum ("zur analyse"), the Bureau of

[6] Andrew, Maddocks and Howat, J. Iron and Steel Inst. (London) **24**, 283 (1931).

Standards' Sibley iron ore and pure ferrous ammonium sulfate were used. For one solution, which at one time or another was standardized against all of these materials, the deviation was less than 0.1 percent.

The samples were dissolved in 10 cc of concentrated HCl to which a few drops of $SnCl_2$ solution had been added. The rate of solution of these oxides being very low even at boiling temperatures, the samples were dissolved at room temperature by allowing to stand over night. This avoided loss of iron by volatilization, spraying, etc. Diphenylamine was used as an internal indicator; the general technique followed was that recommended by Hillebrand and Lundell[7] except that back titration with ferrous sulfate solution seldom proved to be necessary.

The "free iron" content of these samples was not determined. Extensive investigations were made of the Sims and Larson[8] method of removing the metallic iron with copper sulfate and of the Wilner-Merck method as modified by Groebler and Oberhoffer[9] by using mercuric chloride. In agreement with the latter writers, it was found that the copper sulfate method gave high results. Our results indicated, however, that the accuracy of both methods seemed to be influenced by the physical character of the oxide, the degree of subdivision, etc., in an unpredictable way and for this reason attempts to determine the "free iron" were abandoned. Thus in the present work we rely entirely upon the homogenizing annealing treatment to remove any free iron which may have been present in oxides lying within the single phase solid solution area and upon x-ray measurements to determine whether the composition was within the limits of this area. The results of the investigation of the solid solution limits will be reported in another article.

There seemed to be no apparent advantage in separately determining ferrous and ferric iron. It may be remarked, however, that when samples known to contain free iron were dissolved in HCl under rigorously non-oxidizing conditions, the solutions showed by the characteristic yellow color that considerable ferric iron was present.

Silica was determined by solution in HCl followed by double dehydration. The general details followed were those recommended by Hillebrand and Lundell.[10] Four gram samples were used.

Density Measurements

The densities were determined from the loss of weight when the powder was immersed in carefully purified brom benzene. The density of the latter was obtained from the *International Critical Tables* (Vol. 3, page 29). Air was removed by boiling under reduced pressure. Correction was made for the temperature of the liquid.

X-Ray Methods

The x-ray cameras used for making the measurements were of the Seeman-Bohlin type as designed by Phragmén.[11] These cameras were calibrated against carefully purified NaCl using radiations from both iron and copper targets. The value for the length of the cube edge of NaCl was taken as 5.6280A. Only the lines appearing in the camera covering the range where the most deviated reflections appeared ($\sin_2 \theta$ between 0.52 and 0.98 approximately) were used in calculating the lattice parameters of the oxides. Some indication of the sensitivity of these cameras in the present problem has already been given above.

In order to secure a comparison of the intensities of the reflections over the entire range of angles from $\theta=0$ to $\theta=90°$ several photograms were taken in a round Debye camera of 105 mm diameter. The radiation used in all cases was from an iron target in a Siegbahn-Hadding tube with a current of 12–15 m.a. at 45 to 50 kilovolts r.m.s. The current source is a high tension transformer with full wave mechanical rectification. Exposures of about 5 hours duration were required for the outermost reflections.

Results

The experimental determinations of the lattice constants and densities are recorded in Table I together with a number of calculated quantities which will be discussed later. Due to the difficulty of attaining complete equilibrium on the

[7] Hillebrand and Lundell, *Applied Inorganic Analysis*, Wiley, New York, 1929, p. 306, et seq.

[8] Sims and Larson, Ind. Eng. Chem. **17**, 86 (1925).

[9] Reference 5, p. 1986.

[10] Hillebrand and Lundell, *Applied Inorganic Analysis*, Wiley, 1929, p. 540, et seq.

[11] The cameras are described in detail by Westgren, Am. Inst. Min. and Met. Eng., Inst. Mets. Div., 1931, p. 13.

high iron side of the series the results on oxides numbered 6, 7 and 8 are averages of several analyses and lattice constant measurements. The letters *a*, *b*, *c* denote different final annealing treatments.

The sodium chloride structure reported by the earlier investigators is confirmed. The pronounced decrease in the lattice constant as the iron content decreases has not been previously recorded. The shift in the outermost reflections (331 planes) at the two limits of the series is approximately 5 mm. The variation of lattice constant with composition is linear within the limits of experimental error, although a slight downward sag yields the "best fit" (Fig. 1). Because of the short range of composition involved, the use of atomic percent instead of weight percent makes no observable difference. In describing the preparation of these oxides, small amounts of silica were noted. Results on another series of oxides containing approximately 0.9 percent SiO_2 when combined with the present series indicate that the values of a_0 in Table I are subject to corrections due to the presence of SiO_2 which would diminish the values of a_0 by 0.0002A to 0.0008A. Since these corrections lie within the reproducibility limits of the parameter determinations, they will not be further considered.

Discussion

The observed change of the lattice constant with composition is clearly due to some form of solid solution. The next question is what type of solid solution will satisfy the observed data.

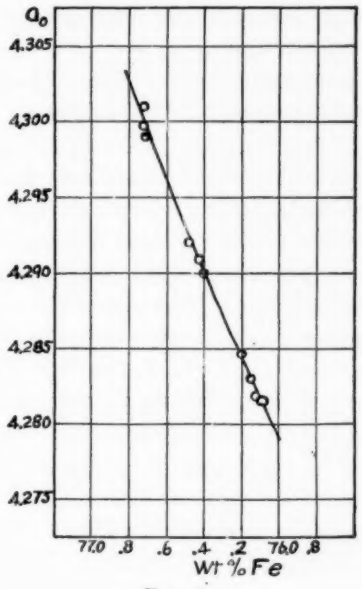

Fig. 1.

Four types of solid solutions are to be recognized as possibilities: (1) The ordinary substitu-

Table I.

Oxide #	1 Weight % Fe	2 Atomic % Fe	3 a_0 in A	4 Density obs.	5 $n_{Fe}+n_0$	6 n_t ($N=8$)	7 Weight % FeO	8 $n_{FeO}+n_0$	9 n_t ($N=4$)	10 N	11 Density calc.	12 $r_{Fe^{++}}$ in A
4 a	76.08	47.68	4.2816	5.613	9.72 $\times 10^{22}$	10.19 $\times 10^{22}$	97.88	5.09 $\times 10^{22}$	5.10 $\times 10^{22}$	3.99	5.622	0.744
4 b	76.07		4.2816									
4 c	76.12		4.2819									
1 a	76.15		4.2831									
1 b	76.20	47.85	4.2847	5.624	9.72	10.17	98.03	5.07	5.08	3.99	5.639	0.777
3 a	76.40		4.2900									
3 b	76.42	48.15	4.2909	5.643	9.72	10.13	98.31	5.04	5.06	3.98	5.667	0.783
3 c	76.48	48.23	4.2920	5.658	9.74	10.12	98.39	5.04	5.06	3.99	5.678	0.784
7 ave.	76.71		4.2990									
8 ave.	76.72	48.56	4.2997	5.725	9.81	10.06	98.70	5.05	5.03	4.01	5.706	0.791
6 ave.	76.72	48.56	4.3010	5.728	9.82	10.02	98.70	5.05	5.03	4.02	5.701	0.791
FeO	77.73	50.00	(4.332	—extrapolated—			100			4.00	5.883	0.816)

tional type in which an atom of one element simply replaces an atom of another in the latter's characteristic structure; (2) the interstitial type in which the foreign atom enters into the interstices of the base lattice; (3) a much rarer form of complex substitution which may take various forms but in any case the number of atoms per unit cell is different from that of the basic lattice; (4) also a rare form in which the lattice of the base substance is changed by the addition of foreign atoms in a more radical way, *e.g.*, from cubic to tetragonal as in the case of the formation of tetragonal martensite.

The fourth possibility may be eliminated at once since it involves the appearance of new lines which have not been observed in the present investigation. To distinguish between the other three, the method of calculating the number of atoms of each kind per unit volume from the density and composition and comparing the sum of these with the number obtained from the structure data seems to be the most convenient. In applying this method[12] we shall first calculate the total number of Fe and O atoms per unit volume and compare this with the number of atoms or lattice points per unit volume of the NaCl lattice. The number of Fe atoms per unit volume is obtained by the relation

$$n_{\mathrm{Fe}}=\frac{dx_{\mathrm{Fe}}}{55.84\times1.65\times10^{-24}},$$

where d is the density, x_{Fe} the weight fraction of Fe, and 1.65×10^{-24} is the weight of a single atom of unit atomic weight. The value of n_0 is obtained in a similar way. The total number per unit volume from the structure data is simply n_t=atoms per unit cell/volume of unit cell $=N/a_0^3$. If $n_{\mathrm{Fe}}+n_0=n_t$ within the limits of experimental error, we have a simple substitution type of solid solution. If $n_{\mathrm{Fe}}+n_0>n_t$ we would assume that the solution was of the interstitial type, while if the sum were less than n_t we should search for some complex form of substitution.

Columns 5 and 6 give the values of $n_{\mathrm{Fe}}+n_0$ and n_t the latter being based on $N=8$, the number of atoms in a unit NaCl cell. It is seen that the actual number of atoms present in a unit volume is from 2.0 to 4.5 percent less than that corresponding to the full number of the NaCl structure. This is considerably beyond the experimental error which is of the order of 0.5 percent and which is due chiefly to the density measurements. Further it may be noted that the sum $n_{\mathrm{Fe}}+n_0$ increases while n_t decreases. The preceding calculation thus eliminates the first two types of solid solution. That something unusual occurs in the solid solution in this particular case was inferred at an early stage of the investigation since either the simple substitution of oxygen for iron or the insertion of oxygen into the interstices of the FeO lattice should lead to an increase in the lattice constant and a decrease was observed. According to Wyckoff and Crittenden[4] the best agreement between the measured and calculated intensities of the diffraction lines is secured when it is assumed that the structure is built up of Fe^{++} and $O^{=}$ ions. The same conclusion may be arrived at from considerations of the radii of the cell constituents. It will be shown later that the lattice dimensions are consistent with those calculated from the ionic radii. The atomic radii lead to very much lower values. We shall, therefore, assume that the lattice is ionic.

As each oxygen is added we must have $2\,Fe^{++}+O\rightarrow 2\,Fe^{+++}+O^{=}$ which is accompanied by a decrease in the ionic radius of the iron ion. Taking the ionic radii as given by Wyckoff[13] $Fe^{++}=0.80$, $Fe^{+++}=0.67$ and $O^{=}=1.35$A, we find that the substitution of an $O^{=}$ for a Fe^{++} would give a net increase of 0.29A and thus cause an expansion of the lattice. For the insertion of an $O^{=}$ in the interstices there would be a much larger expansion, the amount depending upon the position taken in the lattice. While the deformability of the ions has not been taken into consideration this factor alone could scarcely account for the actual decrease observed.

The correct form of substitution seems to be an oxygen for an FeO group.[14] The Fe content is computed over to FeO (Table I), column 7, and the calculation of the number of atoms or, in this

[12] See H. Ott, Wien-Harms Handb. d. Exp. Physik, vol. VII, part 2, p. 283.

[13] Wyckoff, *The Structure of Crystals*, McGraw-Hill, 2d Edition, p. 192.

[14] These FeO groups are merely convenient structural units and have no chemical significance. The iron may actually be in the ferric state.

case, of FeO groups and extra oxygens is made in the same way as before; N in this case is four since there are four FeO groups in the ideal unit cell. The results of these calculations are given in columns 8 and 9. It may be seen that the agreement between the sum $n_{FeO}+n_0$ and n_t is excellent, the maximum difference being less than 0.5 percent. This is further confirmed by the value of N, the number of unit groups in the unit cell, obtained from the equation commonly used for this purpose.

$$N=\frac{a_0^3 d}{(71.84A+16.00B)\times 1.65\times 10^{-24}}$$

in which A and B are the molecular and atomic fractions respectively of FeO and O. Column 11 contains the densities calculated on the basis of $N=4$ which may be compared with the measured values.

The agreement between measured and computed quantities leads the writers to accept the substitution of an oxygen for an FeO group as the correct form of substitution throughout the range of this solid solution. There seems to be no reason for introducing Hüttig's conception of "vagabond oxygen atoms" in this lattice as suggested by Groebler and Oberhoffer.[5]

According to the ordinary interpretation of the thermal diagram, we would regard Wüstite as a solid solution of Fe_3O_4 in FeO, but from the structural standpoint, this interpretation is of doubtful value. The ideal unit cell of FeO contains only 4 FeO groups. Thus to consider the Fe_3O_4 molecule as a substitution unit would be to introduce a molecule or group of practically the same size as the whole cell into which it is to be inserted. If, however, a superstructure of double the observed cube edge were to be found, this idea of molecular substitution might well prove useful. No lines corresponding to such a superstructure have so far been observed in our films. Just how and why it is possible in this special case of solid solution to change the number of atoms per unit cell in this complex way and yet to retain the original type of structure is still to be explained. It might be expected that this type of solid solution in Wüstite, especially since there is likewise a change in electron distribution, would be accompanied by changes in the relative intensities of the lines. Debye photograms of oxides 4 and 6 were identical with respect to intensities as far as visual inspection could determine.

It is evident that the substitution of an oxygen for an FeO group is equivalent to removing one iron. Since the lattice is an ionic one, this means the elimination of an Fe^{++} and thus leaves the unit cell electrically unbalanced by two excess negative charges. This is compensated by the oxidation of 2 Fe^{++} ions to 2 Fe^{+++}. Thus in those unit cells from which an Fe^{++} ion has been removed, each cell will contain 1 Fe^{++}+2 Fe^{+++} +40$^{=}$ or the chemical equivalent of Fe_3O_4. From this point of view the chemical reaction taking place as the oxygen concentration of the phase increased may be formally represented by $4\ FeO \rightarrow Fe+Fe_3O_4$.

There is a general agreement among the various thermal diagrams which have been proposed for the iron-oxygen system, that the FeO-phase (Wüstite) reaches a low temperature stability limit at about 570°C. Below this temperature it decomposes into iron and magnetite. It seems, therefore, that the chemical reaction in the homogeneous solid solution phase as the oxygen content increases is at least formally the same as the decomposition of the FeO. The difference lies in the fact that in the decomposition the rejected iron atoms unite to form the characteristic iron lattice and the remainder the magnetite lattice while in the homogeneous phase the rejected iron appears together with the additional oxygen as new FeO lattices. This point of view is supported by the fact that while the iron content decreases the number of unit cells per gram of iron increases, *e.g.*, for 76.72 percent Fe, the number of unit cells per gram iron is 1.684×10^{21} and for 76.08 percent Fe it is 1.726×10^{21}.

As has already been pointed out, the range of homogeneous solid solutions does not actually include the chemical compound FeO (77.73 percent Fe), but always contains too much oxygen. It is to be mentioned that the results reported in Table I do not necessarily preclude the possibility of actually preparing pure FeO. Preliminary results of an investigation of the homogeneity range at various temperatures, however, indicate that if the compound FeO can exist in the pure state at all, it must be at temperatures above 1300°C.

It is, however, interesting to extrapolate the present results to the theoretical composition of FeO. Various methods of extrapolation were tried but none were found to give particularly satisfactory results due to the fact that the extrapolation range is greater than that of the data. The several methods, logarithmic and others, all gave values of a_0 for FeO (77.73 percent Fe) between 4.329 and 4.334A with 4.332 as a reasonable mean.

In the NaCl structure the shortest distance between neighboring atoms is found along the cube edge. With the extrapolated value of 4.332A for the cube edge of FeO and Wyckoff's value of 1.35 for the radius of the $O^{=}$, the radius of the Fe^{++} ion comes out at 0.816A which compares favorably with Wyckoff's value 0.80. If the distribution of the extra oxygen ions is statistical with a consequently similar distribution of the Fe^{+++} ions we should obtain essentially the same radius for the Fe^{++} ion throughout the series of alloys. In making the calculation we shall assume Wyckoff's value of 0.67A for the radius of the Fe^{+++} ion and obtain the values of the atomic percentages of Fe^{++}, Fe^{+++} and $O^{=}$ from the analyses. The results are given in Table I, column 12.

Considering the general uncertainty in the values of the ionic radii and, indeed, of the concept of a definite ionic radius in the solid state, it would seem that the difference between 0.816 and 0.80A has no special significance. On the other hand, if we may accept Wyckoff's value for $r_{Fe}{}^{++}$ and the assumptions used in calculating the values in column 12, it is possible to arrive at some understanding of the otherwise rather curious lack of stability of the simple compound FeO. On this basis, we would suppose that the simple compound is unstable because the Fe^{++} has too much space available and the characteristic NaCl structure can only exist after the lattice constant has been reduced by the removal of Fe^{++} and the consequent oxidation of other Fe^{++} ions to Fe^{+++} ions to the point where the space available to the remaining Fe^{++} ions corresponds to 0.80A as the limiting radius. It will be seen in column 12 that the oxide containing the highest iron content approximates this value of 0.80A probably within the limits of uncertainty. That the structure is stable at lower iron concentrations where the space available for the Fe^{++} ions corresponds to radii of less than 0.80 is probably to be explained by a small amount of deformation of the oxygen ion. However, the accuracy of the methods available for estimating radii in the solid state do not permit much reliance or emphasis to be laid on arguments of this sort. On the magnetite end, such a treatment is less suitable. Structurally, magnetite is to be considered as $Fe_2^{+++}\ Fe^{++}O_4^{=}$ and if the $O^{=}$ ion retains the radius of 1.35A and is not deformed, the Fe^{++} ion would have a radius of only 0.46A. It is evident that the NaCl structure would become unstable long before such a value could be reached.

A Spectroscopic Study of the Decomposition and Synthesis of Organic Compounds by Electrical Discharges: Electrodeless and Glow Discharges

WILLIAM D. HARKINS AND JOHN M. JACKSON, *George Herbert Jones Chemical Laboratory, University of Chicago*

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In the chemical reactions which occur in electrical discharges through organic vapors and in the maintenance of the discharge, the simple ionization of the molecules, and the resultant formation of clusters, is found to be less important, and the breaking down into molecular, atomic and ionic fragments, more important than has heretofore been supposed. The fragments revealed by the spectroscope are CH, OH, NH, C_2, CN, N_2, CO, CO^+, CS, S_2, H_2, C, C^+, H, and S, and in addition H_2O and NH_3 are known to be formed. When the electrodeless discharge is in benzene vapor the pressure is rapidly lowered until the discharge is extinguished, but this effect is not found with the glow discharge. As compared with the electrodeless discharge, the spectrum from the glow discharge differs in the following respects: the C_2 bands are much less intense and only the fourth group of Swan bands appears appreciably. The line spectrum of C is less intense, and the prominent λ4267 line of C^+ disappears. The CH bands are very clear and that at λ3900 is closer in intensity to that at λ4300 than in the electrodeless discharge. The Balmer series of hydrogen is slightly more intense, and the many-line spectrum of H_2, not present with the electrodeless discharge, is prominent. In general the greatest intensity of the spectrum is given by the cathode glow and the edge of the negative glow near the cathode. The Crookes dark space is a region of very low intensity. The Balmer lines are of nearly uniform intensity throughout except for a specially high intensity just at the cathode. The many line spectrum of hydrogen differs from the others in that it is scarcely visible in the cathode glow. With phenol many bands due to CO and CO^+ dominate the spectrum of the glow discharge, though they are not found in the electrodeless discharge. In the electrodeless discharge the rate and nature of the reaction and the spectrum emitted are affected by the hydrogen to carbon ratio in such a way that the rate of reaction decreases as this ratio increases, and the fraction of gaseous products and the intensity of the spectra emitted by molecules which contain hydrogen increase with this ratio. Thiophene is decomposed into sulfur atoms (S), and molecules (S_2), and carbon monosulfide molecules (CS) in addition to molecules of carbon (C_2) and of monohydrocarbon (CH), atoms of hydrogen (H) and of carbon (C), and ions of carbon (C^+) as had been shown before for the hydrocarbons. In the glow discharge both saturated and unsaturated hydrocarbons are decomposed at about the same rate to form the molecules and atoms listed above. The decomposition products from the glow unite to form brown or black solids somewhat similar to those formed in the electrodeless discharge. From the way in which the product is deposited and the intensity of the spectrum, the reaction is seen to be most rapid at the cathodeward edge of the negative glow.

I. INTRODUCTION

THE chemical changes which take place in electrical discharges through gases have been given a great deal of attention, but are not well known, especially when the gases consist of organic compounds. The present paper and an earlier one from this laboratory, indicate that the simple ionization of the molecules, and the resultant formation of clusters, plays a much less important role than has heretofore been supposed, and that the breaking down of the molecules into molecular, atomic, and ionic fragments, such as OH, CH, NH, C_2, CN, N_2, CO, CO^+, H_2O, CS, S_2, C, C^+, H, S, etc., is much more important in the determination of the products of the syntheses which occur and in the maintenance of the discharge, than has heretofore been supposed.

The chemical effects of electrical discharges through organic vapors have been studied by Lind and his co-workers,[1] Davis,[2] Austin and Black,[3] Linder and Davis,[4] Linder,[5] Brewer,[6] Kinoshita,[7] Kohlschutter and Frumkin,[8] and others.

[1] S. C. Lind and George Glockler, J. Am. Chem. Soc. **50**, 1767 (1928); **51**, 2811, 3655 (1929); S. C. Lind and D. C. Bardwell, *ibid.* **47**, 2675 (1925); **48**, 2335 (1926); S. C. Lind, D. C. Bardwell and J. H. Perry, *ibid.* **48**, 1556 (1926).

[2] A. P. Davis, J. Phys. Chem. **35**, 3330 (1931).

[3] J. B. Austin and I. A. Black, J. Am. Chem. Soc. **52**, 4552 (1930).

[4] E. G. Linder, Phys. Rev. **36**, 1375 (1930); Linder and Davis, J. Phys. Chem. **35**, 3649 (1931).

[5] E. G. Linder, Phys. Rev. **38**, 679 (1931).

[6] A. K. Brewer et al., J. Phys. Chem. **33**, 883 (1929); **34**, 153, 554, 1280, 2343 (1930); **35**, 1281, 1293 (1931).

[7] S. Kinoshita, Phys. Zeits. **8**, 35 (1907).

[8] V. Kohlschutter and A. Frumkin, Ber. **54B**, 587 (1921).

By the use of a mass-spectrograph Stewart and Olson[9] found that hydrocarbons are broken up into shorter chain hydrocarbons by the impacts of the ionizing electrons. Eisenhut and Conrad-Ludwigshafen,[10] also using a mass-spectrograph, obtained parabolas for particles of mass corresponding to C^+, CH^+, CH_2^+, CH_3^+, CH_4^+, and similar fragments with larger numbers of carbon atoms.

In the work reported in the previous paper,[11] benzene and other vapors at pressures of approximately 0.1 mm were subjected to the electrodeless discharge, and decomposed with radiation of brilliant light, to form a resinous deposit on the walls of the discharge flask. A spectrographic analysis of the radiation showed that hydrogen atoms (H), carbon atoms (C), carbon ions (C^+), carbon molecules (C_2), and monohydrocarbon molecules (CH) were present. When oxygen was present in the vapor, molecules of hydroxyl (OH) and carbon monoxide (CO) were found in addition to those above; when nitrogen was present the spectrum also showed molecules of cyanogen (CN) and nitrogen (N_2), singly charged nitrogen ions (N_2^+), and imine molecules (NH).

In the work reported at present a few additional substances were studied in the electrodeless discharge. Some hydrocarbons with a higher ratio of H/C were used in a vain attempt to find any spectrum that might be attributed to dihydrocarbon molecules (CH_2). A sulfur compound, thiophene, gave the spectrum of sulfur atoms (S), sulfur molecules (S_2), and carbon monosulfide (CS) in addition to that shown by benzene.

It was hoped that critical potentials for the disintegration of hydrocarbons and the appearance of the spectra found could be determined by applying various accelerating voltages to the anode of a hot cathode tube filled with a hydrocarbon at low pressure. A visible glow was found to appear at potentials slightly below twenty volts in such a tube filled with benzene vapor, but it was not possible to obtain a glow of sufficient intensity and constancy to make a satisfactory spectrographic analysis, so the method has been abandoned for the present.

A spectrographic analysis of the reactions of hydrocarbons in the glow discharge was considered valuable because the electrical phenomena are better understood than for the electrodeless discharge, and because so much work has been done on the products from such discharges. In the glow discharge as used in this work, without rapid pumping through the discharge, the product is mainly a yellow to black solid wall deposit. Both saturated and unsaturated compounds operated successfully.

The spectrum for hydrocarbons is similar to that for benzene in the electrodeless discharge, except that the spectrum of molecular carbon (C_2) is relatively less intense, and that of ionized carbon (C^+) does not appear at all. The spectrum of hydrogen molecules (H_2) appears, although it does not appear in the electrodeless discharge. For compounds which contain oxygen the spectrum of carbon monoxide (CO) is much more prominent than in the case of the electrodeless discharge.

The intensity of the emitted light was not found to be great enough to prove that all the molecules decomposed are broken up into the particles shown on the spectrogram. However, this is no proof to the contrary, since a part of the radiation from the tube is not in the frequency range studied, and since much of the radiation emitted is absorbed by the gas in the discharge.

II. Apparatus and Procedure

a. Electrodeless discharge

The apparatus used in these experiments is shown in Fig. 1. Here *F* is a 1-liter Pyrex flask which contains the vapor studied. Over the mouth of the flask, a quartz window, *Q*, is attached with De Khotinsky cement. The tube *E*, sealed to the neck of the flask, acts as a trap for any solid product which may be thrown against the window, and, when necessary, as a liquid air trap. Around the flask in the plane passing through the window, is tightly wound a vertical coil of six turns of insulated, heavy copper wire. In addition to this coil, the high-frequency circuit consists of a 1 k.v.a. Thordarson transformer, *V*, which supplies 25,000 volts maximum, a spark

[9] H. R. Stewart and A. Olson, J. Am. Chem. Soc. **53**, 1236 (1931).

[10] H. O. Eisenhut and R. Conrad-Ludwigshafen, Zeits. f. Electrochem. **36**, 654 (1930).

[11] W. D. Harkins and D. M. Gans, J. Am. Chem. Soc. **52**, 5165 (1930).

gap, *S*, capable of adjustment by a screw and made of cylindrical zinc electrodes 1.7 cm in diameter, and a 0.00025 microfarad condenser, *C*. The frequency of the circuit, as determined by a radio receiver, was about 800 kilocycles per second.

An n-dibutyl phthalate vapor pump, *P*, which is backed by a Cenco Hyvac pump, is used instead of the mercury vapor pump used in the previous

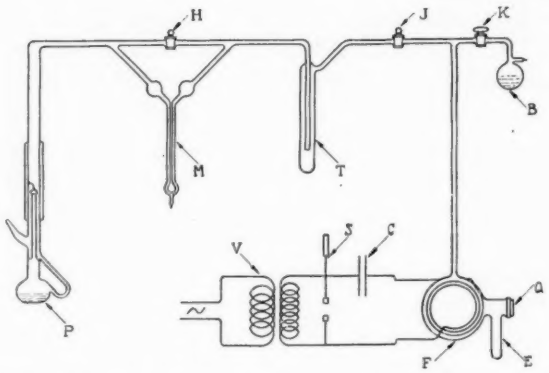

FIG. 1. The experimental arrangement for experiments with the electrodeless discharge.

work, so that all mercury might be kept out of the apparatus. Pressures are read by means of the manometer, *M*, which is filled with the n-dibutyl phthalate liquid. The differences in level are read against a millimeter scale with a magnifying lens. They can be read accurately to less than a millimeter of the liquid used, which is equivalent to 0.073 mm of mercury. By closing stopcock *H* the difference in pressure between the line side and the pump side is registered, the pressure on the pump side being taken as zero for the purposes of these experiments. The trap, *T*, can be used to keep the n-dibutyl phthalate vapor out of the flask and to keep the reacting substance out of the pumps.

The compound to be studied, properly purified and dried, is distilled under reduced pressure into the bulb, *B*, which is then sealed except for the outlet through stopcock *K*. The apparatus is then completely evacuated, the stopcock *J* is now closed, and kept closed permanently except during pressure measurements. The electrodeless discharge is now started, and the vapor admitted through *K* to the flask, where it is decomposed to form the solid product with the emission of light. The discharge is very sensitive to pressure changes, so that the stopcock *K* must be adjusted very carefully. The discharge causes a considerable evolution of heat, which is dissipated with a fan.

In the case of methane the apparatus is slightly modified, so that the vapor from the methane, which is condensed in a bulb immersed in liquid air, is led into the flask, *F*, through a side arm, and continuous pumping through the stopcock *J* is maintained.

The light which passes out through the quartz window, *Q*, is focused on the slit of a spectrograph. In this work a Hilger E 1 quartz spectrograph and a Steinheil GH glass spectrograph were used. A small plane silver mirror, placed when desired at an angle of 45° just in front of the quartz window, throws the spectrum of an iron arc on each plate, for comparison. For the work in the visible region, panchromatic plates were used. The deposit of a firmly adhering film of product necessitated a change of the window after each exposure, which lasted from one-half to several hours.

b. Glow discharge

The vacuum line used in these experiments is the same as that shown in Fig. 1, the discharge tube and electrical circuit are shown in Fig. 2.

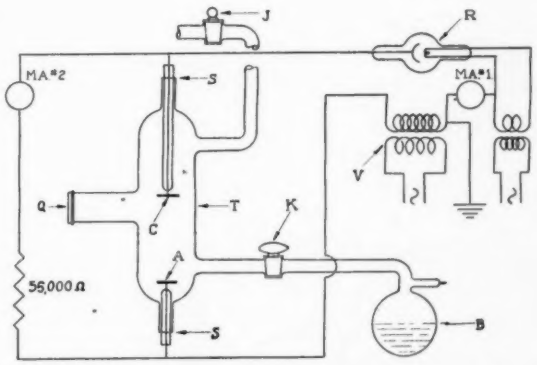

FIG. 2. The experimental arrangement for experiments with the glow discharge.

The discharge tube, *T*, is equipped with both inlet and outlet tubes, so that vapor may be pumped continuously through the discharge. The quartz window, *Q*, is sealed on to the side arm with wax. The electrodes *C*, cathode, and *A*, anode, are aluminum disks 2 cm in diameter and 1.5 mm thick, which are clamped to tungsten

leads sealed into glass tubes. These tubes fit into tubes at the ends of tube T, so that the electrode position may be adjusted at will. When the electrodes are in the desired position, vacuum tight seals are made at the joints, S, with picein wax. An electrode spacing of about 8 cm is used, the cathode being placed so that light from the cathode glow and negative glow come directly through the window.

In addition to the electrodes the electrical circuit consists of the 25,000 volt maximum, 1 k.v. a. transformer, the output of which is rectified by a single kenetron, R. The current flow is measured with a Weston d.c. milliammeter, No. 1, on the assumption that the reading represents the average for the half cycle in which current flows. The milliammeter No. 2 and 56,000-ohm resistance are shunted across the electrodes to measure the voltage drop. This was done in only one special experiment.

After evacuation of the system, the vapor is admitted to the tube, T, through stopcock K to a pressure of about 2 millimeters of mercury. The glow discharge is then started with a potential difference of 500 to 1,000 volts between the electrodes, and the vapor decomposes to form the solid product. A blue or green light is emitted in the familiar regions cathode glow, negative dark space, and negative glow. The positive column usually does not appear under the conditions of electrode spacing and pressure used, at higher pressures a striated positive column appears. The discharge is of the abnormal type, i.e., the current passed, which registers as 35 to 40 milliamperes, is greater than that required to make the glow completely cover the surface of the cathode. The discharge is accompanied by a considerable heating of the walls of the tube, and a fan is used for cooling.

The discharge is not particularly sensitive to pressure changes, but a pressure of about 2 millimeters which gave a dark space width of 1.5 or 2 millimeters was used throughout the work. With the saturates a continuous pumping through J is required in order to allow fresh vapor to flow into the discharge; with the unsaturates pumping is not required.

The tube is mounted vertically and the light which comes through the window is focused on the slits of the spectrographs mentioned above, in such a way that the images of the cathode glow, negative dark space, and negative glow fall in different positions on the slit. This facilitates a comparison of the different regions of the discharge on one spectrogram. Panchromatic plates were not used in this work because they are rather slow, and several hours of exposure were required at best. The line $H\alpha$ is all that is lost in this way. Exposures of four or five hours were required; the window was cleaned between exposures.

The intensity of the light radiation is measured by means of a Kipp thermopile and Weston galvanometer, which were calibrated with a Bureau of Standards standard radiator. A quartz cell filled with distilled water is placed in front of the thermopile to filter out infrared radiation. The discharge is carried out in a quartz flask instead of the tube described above. Readings are taken at various points around the flask, before much deposit forms on the walls, then the total radiation is calculated by integrating over the whole surface.

III. Purification of Compounds

The compounds studied in the electrodeless discharge were xylene, mesitylene, methane, pyridine, benzaldehyde, and thiophene. The methane was prepared by heating a mixture of sodium acetate and barium oxide, the gas being collected over water. The gas was then passed through a trap surrounded by solid carbon dioxide, bubbled through concentrated sulfuric acid, passed over phosphorus pentoxide, and condensed in a trap, connected as bulb B, which was surrounded by liquid air. With the other compounds, the purest reagents available were dried over sodium, barium oxide, phosphorus pentoxide, or anhydrous sodium sulfate, and a middle fraction distilled into the bulb B under reduced pressure.

The compounds studied in the glow discharge were benzene, n-heptane, methane, pyridine, and phenol. The purification or preparation was as above except in the case of methane. The methane was prepared in small quantities by heating the reagents mentioned above, in the closed evacuated system, the gas being immediately condensed in a trap surrounded by liquid nitro-

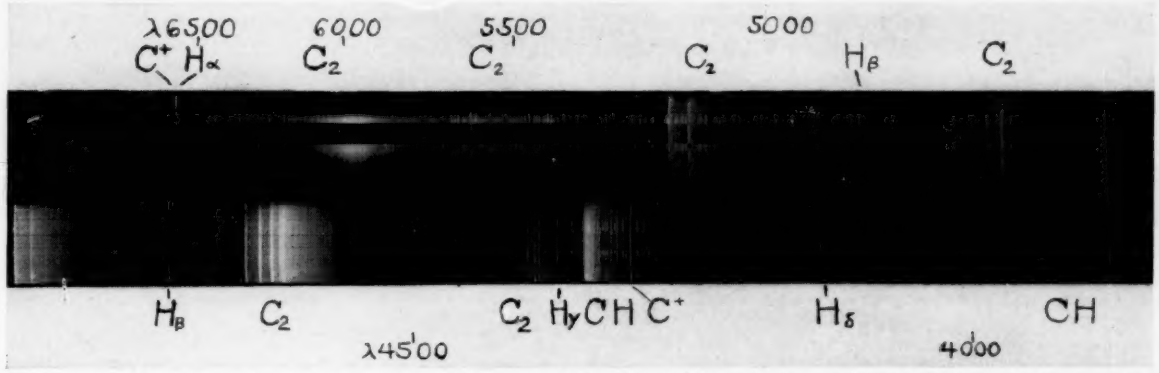

FIG. 3. Spectrum from the decomposition of benzene in the electrodeless discharge (by Gans). It was taken on the Steinheil spectrograph and shows the spectrum of the Fe arc for comparison.

gen. The gas was then dried and purified by repeated distillation over phosphorus pentoxide from one trap to another.

IV. EFFECTS OF THE ELECTRICAL DISCHARGES

a. Electrodeless discharge

(*1*) *Benzene, xylene, mesitylene and methane.* (Fig. 3.) The hydrogen to carbon ratios of these substances are, respectively, 1.00, 1.25, 1.33, and 4.00. Consequently there should be a definite trend of characteristics in the reaction as the vapor is changed from benzene[12] to xylene and mesitylene and to methane. In the case of benzene several thousand liters of the vapor were admitted to the discharge flask in the course of a half hour and decomposed to form a solid product. No cooling agent was required around the trap *E*, and not only did the pressure remain constant during the decomposition, showing no accumulation of permanent gas, but if at any time the inflow of fresh vapor was stopped, the pressure was reduced by the discharge to the point of extinction.

In the cases of both xylene and mesitylene the discharge ran continuously for long periods without the accumulation of enough permanent gas to stop the discharge. However, in contrast to the benzene, the discharge did not reduce the pressure sufficiently to extinguish itself when the inflow of either of these substances was stopped. Thus the condensation is less complete than that with benzene. The differences between xylene and mesitylene are not great enough to be observed in the reaction, but the rate of formation of product was slightly less for mesitylene than for xylene, which in turn was less than that for benzene (1.2 grams per hour). The products from both substances are light brown in color and consist mainly of a loose powdery material, with some scaly material which clings to the walls of the flask.

The initial discharge is a greenish-white ring which turns into a white glow. The glow completely fills the flask at lower pressures, but has a non-luminous core at higher pressures. When the discharge is allowed to run without the inflow of fresh vapor the glow becomes very red, which shows that the spectrum of the α-line of the Balmer series of hydrogen has been greatly enhanced.

These data are summarized for all of the substances in Table I. The first column gives the color of the initial ring discharge, the second that of the glow. The third column gives the maximum pressure at which the discharge will operate when a spark gap of approximately 1.5 centimeters is used in the electrical circuit. This length and these pressures are somewhat greater than those actually used in the continuous runs. Column 4 states the color of the product, column 6 the physical form of the product, and the last column gives the approximate rate of formation of the solid product in grams per hour at the intermediate pressures used in the continuous runs.

With methane the pressure was found to rise slightly when the discharge was run through fresh vapor with both inlet and outlet from the flask closed. It was impossible to run the discharge with a continuous inflow of the methane

[12] Reaction of benzene described in the previous paper. (Reference 11).

TABLE I.

Substance	Color of discharge Ring	Color of discharge Glow	Max. press. 1.5 cm gap	Color of product	Form of product	Rate of formation of product, g per hour
Xylene.....	Greenish-white	White to red	0.26 mm	Light brown	Powder and scales	1.0
Mesitylene.....	Greenish-white	White to red	0.30	Light brown	Powder and scales	0.8
Methane.....	Greenish-white	White to red	1.01	Light brown	Scales	0.0
Pyridine.....	Greenish-blue	Bluish-white to brown	0.28	Dark brown	Powder and scales	1.8
Benzaldehyde....	Greenish-blue	Blue and red to red	0.37	Dark brown	Powder and scales	1.2
Thiophene.....	Intense green	Purple to red	0.19	Dark brown to black	Some powder and heavy scales	0.7

unless the gaseous products were continuously pumped out. This is the kind of pressure effect that might easily have been predicted by observing the hydrogen to carbon ratio. Thus, the greater the value of H/C, the less complete is the condensation to a solid of very low-vapor pressure.

The photographs of the decomposition spectra of all three hydrocarbons are very much like those published for benzene in the previous paper. All five groups of the Swan bands are prominent, and the other groups of C_2 bands from λ4102 to λ3998 are present. The CH bands at λ4300 and λ3900 are both prominent, and the first five lines of the Balmer series of hydrogen are very strong. The line spectrum of C^+ and the line from the arc spectrum of C at λ2478 were also observed to be strong. The relative intensities for these and the other substances are tabulated in Table II. The figures are only approximate, and do not hold for a comparison between substances. The very long exposures gave a much greater blackening of the plate than is indicated by the table. The times of exposure given are for the visible and near ultraviolet position on the Hilger instrument. Except in the case of unusually long exposures in this position, the exposures in the second position, λ3200 to λ2400, were about twice as long.

TABLE II. *Relative intensities.*

	Substance					
Exposure, hrs.	Xylene 0.5	Mesitylene 5.5	Methane 3	Pyridine 1	Benzaldehyde 1	Thiophene 1
Intermediate decomposition product						
CH.....	4	4–5	3–4	3	3	3
Swan C_2...	4	4–5	2	3	3	3
All other C_2.	2	3	1	1	0–1	0–1
C^+(C)....	3	2–3	4	3	4	3–4
H.....	4–5	4–5	5	4	4	4
CN.....				5		
NH.....				3		
N_2.....				2		
N_2^+.....				2		
CO.....					1	
OH.....					2	
S.....						4
S_2.....						3
CS.....						5

Key: 1, Very weak; 2, weak; 3, average; 4, intense; 5, very intense.

As was expected, the intensities of the spectra of H and CH become greater as the value of H/C is increased. However, even with long exposures, no new bands appeared, and it must be concluded that if any CH_2 molecules are present, they are present in such small concentrations that their radiation in the region investigated is negligible in comparison with the radiation identified.

(*2*) *Pyridine.* The decomposition of pyridine, in contradistinction to the aniline described in the previous paper, went on continuously without the necessity of using a cooling agent on the side tube *E*. The difference between the behavior of aniline and pyridine must depend in part on the hydrogen to carbon ratios which are 1.17 and 1.00, respectively. Of course, the presence of the nitrogen atom is an additional factor which influences the behavior of both substances. The product from pyridine had a strong odor of bivalent carbon compounds, but did not give the positive litmus test for ammonia, which was found with aniline.

In addition to the spectrum shown by the hydrocarbons, the spectrogram showed the violet cyanogen bands from group II at λ4532 to group V at λ3590 very prominently. The β bands of NH at λ3360 and λ3370, the second-positive group of

N_2 at λ3577, λ3371, and λ3159, and the first-negative group of N_2^+ at λ3914 were also found to be present. Thus the spectrum is like that due to the aniline decomposition except that the bands due to C_2 and CH are relatively a little less intense.

(*3*) *Benzaldehyde.* The ratio of hydrogen to carbon is 0.86 for benzaldehyde, whereas, it is 1.00 for phenol. It is not surprising that the decomposition of benzaldehyde will run continuously without the use of a cooling agent on *E*, although liquid air was required to condense out the water vapor formed in the decomposition of phenol described in the previous paper.

The spectrum is similar to that for phenol except that the CO bands at λ2974 and λ2832 are relatively a little stronger and the OH band at λ3064 a little weaker. The rest of the spectrum is similar to that from the hydrocarbons.

(*4*) *Thiophene.* Continuous decomposition was easily maintained as, for example, in the case of benzene. The product had a very dark color with a sort of metallic lustre, and most of it clung tenaciously to the walls of the flask. The color effects in the discharge were very beautiful, since there was much purple and red in the glow.

In addition to the spectrum shown by the hydrocarbons the spectrogram showed the line spectrum of S very prominently, and the band spectrum of S_2. A very striking set of bands extending from about λ2850 to λ2460 was found. They are due to CS, and the appearance of the plate was much like that of one published by Martin.[13] The bands were later analyzed and discussed more fully by Jevons.[14]

b. Glow discharge

(*1*) *Benzene.* (Fig. 5.) The discharge ran continuously without pumping out any gaseous products or using condensing traps, and at the pressures used the pressure was found to decrease somewhat when the discharge was passed without the inflow of fresh vapor. However, the effect of the reaction differed from that found in the electrodeless discharge in the fact that the discharge would not reduce the pressure to the point of extinction. The product formed at first in a dark brown band on the walls of the tube in the region of the cathode. This film spread all over the tube, being lighter in color behind the electrodes. Later black spots appeared in it, and at the end of a number of hours of continuous running a considerable amount of gray black material, much like asphalt in appearance, was found in the tube, the original brown and yellow film being confined to a thin layer on the wall. None of the product was found loose as in the electrodeless discharge, though most of it could be scraped off the wall easily, but some clung very tightly. An analysis of the product gave $(C_{1.00}H_{0.89})_n$ as its average composition. The loss of one-tenth part of hydrogen is surprising, but was probably due to occasional pumping out through *J* to reduce the pressure, necessitated by improper regulation of the inlet *K*.

The solid product was formed at a rate of approximately 0.5 gram per hour, which is equivalent to the conversion of 0.00645 mole of benzene into a solid of the composition given above in the course of an hour. Since by the assumption used in measuring the current, the current was passed at a rate of 17.5 milliamperes, registering as 35, or 0.000655 equivalents of current per hour, there were 9.87 moles of benzene decomposed for every equivalent of current passed.

In measuring the intensity of the light radiation there was found to be a great deal of infrared radiation from the hot walls of the flask, and possibly some from vibration-rotation bands. This was successfully filtered out with a quartz cell filled with distilled water, which was found to give very good transmission in the blue region, where most of the light radiation lies. The values found are only approximate because the deflection was only a few millimeters on the scale of the galvanometer used, and because the fraction of transmission by the walls of the discharge flask and the filter was not known. From the spectrograms taken the average wave-length of the radiation was estimated to be 4200 angstroms. The total radiation in the region measured was found to be at the rate of 4.98×10^{-3} watt, which is equivalent to 1.07×10^{16} quanta per second. This means that there were approximately 102 molecules of benzene decomposed for each quantum of energy radiated through the quartz in this region.

[13] W. B. Martin, Proc. Roy. Soc. **A89**, 121 (1913); plate 6, No. 4.

[14] W. Jevons, Proc. Roy. Soc. **A117**, 351 (1927).

TABLE III.

Substance	Color of discharge	Color of product	Form of product	P.D. in volts	Rate of formation of product (g per hr.)	Moles per equiv. of current	Molecule per quantum of radiation
Benzene . .	Blue-green to white	Black to yellow	Powder and gum	800	0.5	9.87	102
n-heptane.	Blue-green to pink	Black to brown	Powder	800	0.15	2.47	25.5*
Methane. .	Blue-green to pink	Black to brown	Powder	450 to 650	0.03	3.28	38.2*
Pyridine. .	Blue to violet	Black to brown	Powder and scales	800	0.14	2.75	
Phenol. . . .	Blue-green	Black to brown	Powder and scales	650	0.16	2.40	

* Estimated assuming radiation equal to that from benzene decomposition.

These data are summarized in Table III. The first column gives the color of the discharge, the second the color of the product, and the third the physical form of the products from the different substances. Column four gives an approximate value of the potential difference across the discharge, which was estimated by a comparison of the observed average value of the current with a curve for current against voltage. This curve had been obtained by varying the pressure during an experiment in which the voltage and current were both measured. Column five presents the rate of formation of solid product in grams per hour, column six the rate of conversion of the original vapor to solid in moles per equivalent of current passed, and the last column shows the rate of conversion in terms of molecules per quantum radiated through the quartz.

The spectrum obtained was generally similar to that of benzene and other hydrocarbons in the electrodeless discharge, but there are a number of noteworthy differences. The C_2 bands are much less intense and only the fourth group of the Swan bands appears appreciably. The line spectrum of C is less intense, and the λ4267 line of C^+, which is very prominent in the electrodeless discharge, does not appear at all. The CH bands are very clear, that at λ3900 possibly being closer in intensity to that at λ4300 than in the electrodeless discharge. The Balmer series of hydrogen appears to be a little more intense, and the many line spectrum of H_2, which was not found at all in

TABLE IV. *Relative intensities for glow and electrodeless discharges.*

	Substance									
	Benzene		n-heptane		Methane		Pyridine		Phenol	
Exposure, hrs.	*G* 4	*E** 0.5	*G* 5	*E** 0.5	*G* 3.5†	*E* 3	*G* 4	*E* 1	*G* 2†	*E** 1.5
Intermediate decompos. product										
CH.	4	4	4	2	4	3	3	3	2	3
Swan C_2.	3	5	3	0	0	2	1	3	2	3
All other C_2.	2	2	2	0	0	1	0	1	0	2
C.	1	3	1	1	?	3	3	3	4	3–4
C^+.	0	3	0	1	0	0	0	3	4	3–4
H.	5	4	5	5	5	5	4	4	4	3
H_2.	3	0	4	0	4–5	0	1	0	1	0
CO.									4–5	1
CO^+.									4–5	0
OH.									3	3
CN.							5	5		
N_2^+.							4	2		
N_2.							0	2		
NH.							3	3		

Key: 1, Very weak; 2, weak; 3, average; 4, intense; 5, very intense.

* Data taken from previous paper (reference 11). Heptane is not a fair comparison because there was no pumping out in the electrodeless experiment.

† Time is for Steinheil instrument, others are for Hilger.

the electrodeless discharge, is very clear in the spectrum of the glow. The relative intensities are summarized in Table IV, where they are compared with those in the electrodeless discharge.

The spectrum indicates the existence of the intermediate decomposition products C and H atoms, C_2, CH, and H_2 molecules in the glow discharge through benzene vapor.

The variations in intensity, as one looks up and down the spectrum lines across the different parts of the discharge, are of interest. Most parts of the spectrum vary in the same manner, the most intense regions are the cathode glow and the edge of the negative glow toward the cathode, the Crookes dark space is a region of very low intensity, and there is some fading out as one goes from the edge out into the negative glow. The Balmer lines show fairly uniform intensity throughout except for a very intense and blurred tuft just at the cathode. The many line spectrum of hydrogen differs from the rest in that it is scarcely visible in the cathode glow, and grows more intense as one progresses into the negative glow. A spectrogram taken of the region considerably farther out into the negative glow was similar to that portion of the negative glow a few millimeters from the edge except for a general decrease in intensity. The above data are summarized for all of the substances in Table V, where a comparison of intensities is made for the regions of the cathode glow,

TABLE V. *Relative intensities in different parts of the discharge.*

Intermediate decomposition product	Substance														
	Benzene			n-heptane			Methane			Pyridine			Phenol		
	a	*b*	*c*	*a*	*b*	*c*	*a*	*b*	*c*	*a*	*b*	*c*	*a*	*b*	*c*
CH	4	3–4	3	4	3–4	3	4–5	4	4	3	2	1	2	1	0–1
Swan C_2	3	3	2	3	3	2	0	0	0	1	1	0–1	2	1	0
All other C_2	1	2	1	2	2	1	0	0	0	0	0	0	0	0	0
C	1	1	0	1	1	0	?	?	?	3	3	2	5	4	3
C^+	0	0	0	0	0	0	0	0	0	0	0	0	4	4	4
H	5	5	5	5	4	4	5	4–5	4–5	4	4	3	4–5	4	4
H_2	0–1	3	3	1	4	4	4–5	4–5	4–5	0–1	1	1	1	1	1
CO													5	4	3
CO^+													4	4	4
OH													3	2	1
CN										5	5	5			
N_2^+										3	3	4			
NH										3	3	3			

Key: *a*, Cathode glow; *b*, edge of negative glow; *c*, negative glow about 5 mm from edge. 1, Very weak; 2, weak; 3, average; 4, intense; 5, very intense.

the edge of the negative glow, and that portion of the negative glow a few millimeters from the edge.

(*2*) *n-heptane.* As would be expected, there was found to be a large quantity of gaseous product formed in the decomposition of heptane, which was shown by a large increase in pressure when the discharge was run through fresh vapor with both inlet and outlet closed. Constant pumping out was employed in the continuous runs, and a solid product very much like that from the benzene in appearance was obtained. Analysis showed that the hydrogen content of the product is slightly greater, the average composition being $(C_{1.00}H_{1.13})_n$.

The spectrum was found to be similar to that from the benzene except for a small increase in the intensity of the many line spectrum of hydrogen.

(*3*) *Methane.* (Fig. 5.) Although the percentage of gaseous product must be greater in this case than for the heptane, the pressure increase in the closed system was much less noticeable on account of the smallness of its molecules. The rate of formation of product was very slow, a brown film, with some black on the interior, was formed. The average composition of the solid was found by analysis to be $(C_{1.00}H_{1.25})_n$. The analyses of the products from benzene, heptane, and methane show that the composition of the product is directly influenced by the hydrogen to carbon ratio of the reacting substance.

The spectrum is interesting in that the C_2

bands disappeared altogether, and the spectrum of H_2 became very strong.

(*4*) *Pyridine.* The characteristics of the operation were very much like those for benzene, except that the discharge had a great tendency to jump back to the glass tube holding the cathode as soon as some product had formed on this tube. This heated the glass so much that small holes developed, and a great deal of trouble was experienced in keeping the apparatus vacuum tight.

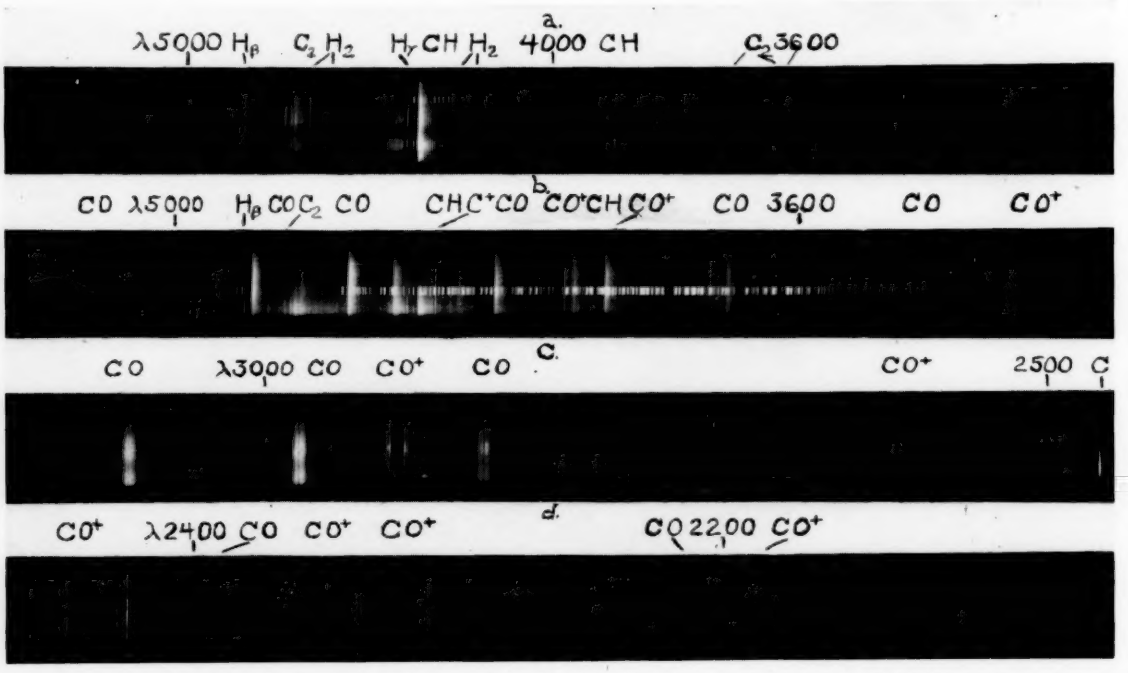
a.
λ5000 Hβ C2 H2 Hγ CH H2 4000 CH C2 3600
b.
CO λ5000 Hβ CO C2 CO CHC+CO CO+CH CO+ CO 3600 CO CO+
c.
CO λ3000 CO CO+ CO CO+ 2500 C
d.
CO+ λ2400 CO CO+ CO+ CO 2200 CO+

FIG. 4a. Spectrum from the decomposition of benzene in the glow discharge, as taken by the Hilger spectrograph, using the iron arc for comparison. b, c, d. Spectra from the decomposition of phenol in the glow discharge. Hilger spectrograph.

The product was more scale-like in character and clung tightly to the glass walls. It had a strong odor of bivalent carbon compounds.

The spectrum differed from that in the electrodeless discharge in the decrease in intensity of the spectrum of C_2, the disappearance of that of C^+, and the presence of a spectrum due to H_2. The first negative group of N_2^+ shows at λ4278 and λ4237 in addition to the band at λ3914, which was the only one showing in the electrodeless discharge. The cyanogen "tail" bands[15] are quite prominent in the glow discharge, but very faint in the electrodeless discharge.

(*5*) *Phenol.* (Fig. 4.) The operation was not very satisfactory, since the vapor pressure of phenol at room temperature was lower than that needed for the best operation of the discharge. However, sufficient decomposition and satisfactory operation for the spectrograph were obtained by the use of a heating bath around *B*. There appeared to be a slight rise in pressure when the discharge was run through the fresh vapor in the closed system. Constant pumping out was used to insure the inflow of fresh vapor. The product formed slowly, but had an appearance much like that from the hydrocarbons.

The spectrum differed from that of the other substances in the glow discharge by the appearance of the line due to C^+ at λ4267, the relative decrease in intensity of the spectrum of H_2, and the complete domination of all the region investigated by a great many bands due to CO and CO^+, which had not been found in the electrodeless discharge. These bands are the angstrom bands of CO, the third and fourth positive groups of CO, the first negative group of CO^+, the comet-

[15] A. S. King, Astrophys. J. **14**, 323 (1901).

tail[16] bands of CO^+, and the Baldet-Johnson[17] bands due to high pressure CO^+. Bands at λ4830, λ3895, and λ3679, which were first reported by Duffendack and Fox[18] and thought to belong to the angstrom system, were quite prominent. There was a fairly prominent band at λ4664, which was not identified in a fairly exhaustive search of the literature, but which was much like the angstrom bands in appearance.

V. Discussion

In the electrodeless discharge there are two electrical fields, one an alternating electrical field, parallel to the axis of the solenoid, and the other an electromagnetic field whose electrical energy is in rings perpendicular to the axis of the solenoid. Both fields may play a part in the discharge reaction, but the electromagnetic field must be most important in the initial ring discharge, and electrostatic field parallel to the axis most important in the glow which comes later. The pulsating d.c. electrostatic field between the electrodes in the glow discharge is comparable to the field responsible for the glow in the electrodeless discharge.

The differences between the reactions in the two discharges, which are shown by differences in their spectra and products, must depend on the differences in pressure and electrical fields. For instance, it is conceivable that more collisions favorable for the combination of hydrogen atoms into molecules take place at the higher pressure in the glow discharge than in the electrodeless discharge, thus accounting for the appearance of the many line spectrum of hydrogen in the glow discharge. The Baldet-Johnson high-pressure bands of CO^+ may appear in the one rather than the other, not only because of the pressure difference, but also because of a possible difference in electron energy, since energies of the order of one hundred electron volts are required for the appearance of these bands.

[16] A. de la Pluvinel and F. Baldet, Astrophys. J. **34**, 89 (1911).

[17] Baldet, Comptes Rendus **178**, 1525 (1924); Johnson, Proc. Roy. Soc. **A108**, 343 (1925).

[18] O. S. Duffendack and G. W. Fox, Astrophys. J. **65**, 214 (1927).

It is probable that the energy of electron impact is the most important factor in the smashing of the molecules of the original substance into the spectroscopically observed intermediates. There must be many positive ion impacts, but evidence points to the fact that they are quite ineffective until they acquire velocities comparable to the electron velocities required to produce dissociation or ionization,[19] velocities which they almost certainly cannot acquire. Collisions of the second kind no doubt play an important part in the reaction. The fact that the rate of reaction is most rapid, and that one of the most intense portions of the spectrum is located at the edge of the

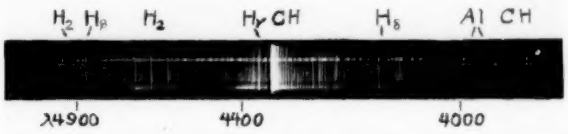

Fig. 5. Spectrum from the decomposition of methane in the glow discharge, with the iron arc reference spectrum taken on the Steinheil instrument.

negative glow, where the density of high velocity electrons is greatest, points to the importance of electron impacts in the reaction.

While there is no direct evidence that all of the molecules are smashed into the intermediates found, it seems probable that most of them are so decomposed, or at least that these active particles initiate the most of the reaction. Certainly the energy available, about 80 electron volts per molecule of benzene reacting and more for the other substances, should be sufficient for the breaking up of all the reacting molecules. The breaking up of a molecule may take place directly by electron impact, there may be ionization or excitation by electron impact followed by dissociation, or the ionization or excitation may be due to collisions of the second kind, or to radiant energy, and again be followed by dissociation.

In conclusion, it must be stated that the phenomena in reactions of this type are so complicated that it would be foolish to postulate any definite mechanism as being responsible for the reaction.

[19] Compton and Langmuir, Rev. Mod. Phys. **2**, 123 (1930).

Chemical Aspects of the Infrared Absorption Spectra of the Ethyl Halides

PAUL C. CROSS AND FARRINGTON DANIELS, *University of Wisconsin*

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The infrared absorption spectra of ethyl chloride, ethyl bromide and ethyl iodide have been determined with a prism spectrometer between 1.5μ and 15μ. Eight experimentally observed fundamental frequencies have been selected which, together with their first harmonics and simple combinations, are shown to account for the entire spectrum. A type of vibration between atom pairs believed to represent the important feature of the motion of the atoms is suggested for each of these fundamentals. The shifts in the absorption maxima produced by the substitution of the different halogens together with absorption and Raman data of related compounds are used in selecting these types of vibration. The bearing of these hypotheses on problems in chemical kinetics is discussed.

IN connection with an extended study of the decomposition of ethyl bromide and related compounds in this laboratory, it was decided to investigate other phenomena connected with the motion of the atoms in the molecule. Remarkable advances in this field have been made through the study of infrared spectra of simple molecules[1] as a result of new mathematical concepts, improved apparatus, and an unexpected wealth of Raman data. Although the more complex molecules such as ethyl bromide cannot yet be subjected to exact mathematical treatment, many useful empirical deductions can be made, and the study of their spectra should not be postponed because of the inability to make a rigorous interpretation in terms of the latest theories. The complicated molecules are often more interesting from a chemical standpoint.

The authors have sought to determine and analyze the infrared absorption spectra of ethyl chloride, ethyl bromide and ethyl iodide from 1.5μ to 15μ. They have endeavored to determine the fundamental frequencies of vibration which combine to form the whole vibrational spectrum, and to associate with each a characteristic type of motion between specific atoms.

The spectrometer used did not permit the observation of the rotational fine structure of the absorption bands (nor was this desirable for the present purpose) but it gave with sufficient precision the positions of the bands and their approximate relative intensities. In the compounds studied, the spectra were quite similar, the bands in general shifting toward lower frequencies with increasing weight of the halogen. Some of the bands shifted more than others and it is logical to attribute the bands with the larger shifts to atom motions in the molecule which directly involve the halogens.

The first attempt at analysis of a system as complex as the ethyl halides is likely to be incomplete. The solution of certain mathematical problems would be of great help, but it must be remembered that the results of such calculations are no more reliable than the assumptions upon which the mathematical operations are based.

APPARATUS

The spectrometer was constructed by the authors with the help of Mr. Lee Henke, mechanician of the Chemistry Department. It employs the Wadsworth mounting of prism and plane mirror and is equipped with a 60° rocksalt prism having faces 6 cm square. The energy is measured by a Moll thermopile and a Cambridge Paschen-type galvanometer.

The spectrometer was calibrated[2] for 25° with refractive indices from Paschen[3] and temperature coefficients from Liebreich.[4,5]

The standard wave-length used for calibration was the 4.26μ band of carbon dioxide in the atmosphere. Although this band is somewhat dif-

[1] Dennison, Rev. Mod. Phys. **3**, 280 (1931).

[2] Complete details will be given in another communication.

[3] Paschen, Ann. d. Physik **26**, 120 (1908).

[4] Liebreich, Verh. d. D. Phys. Ges. **13**, 700 (1911); **13**, 1 (1911).

[5] Schaefer and Matossi, *Das Ultrarot Spectrum*, page 47, Julius Springer, Berlin, 1930.

fuse, it is very convenient to use and it is located in the region studied. The setting of the spectrometer was checked at frequent intervals during a measurement by reference to this band.

The spectrometer is capable of measuring absolute wave-lengths with an accuracy of $\pm 0.02\mu$ and wave-length differences between ethyl bromide and iodide with an accuracy of $\pm 0.005\mu$, except in the region of the longer wave-lengths.

Determination of Spectra

The results are shown in Figs. 1 and 2 in which transmissions in percent are plotted as ordinates and wave numbers (cm^{-1}) as abscissas. Curves *A* represent the transmission of 1.5 mm thicknesses of liquid ethyl bromide and ethyl iodide. These were run simultaneously with the aid of a device which permitted putting each liquid cell and a blank cell successively into the beam of radiation at each position of the spectrometer table. Curves *B* are for liquid layers 0.05 mm in thickness. Curves *C* are for the vapors at their respective vapor pressures at 25°, in a gas cell 16 cm long. Curves *D* were taken at undetermined reduced pressures to show more accurately the positions of maximum absorption. Curve *E* for ethyl chloride was taken at atmospheric pressure. Curve *F* on ethyl bromide shows the transmission of a 0.5 mm layer of the liquid. The cells were made of glass tubes or mica sheets to which rocksalt windows were attached with LePage's fish glue.

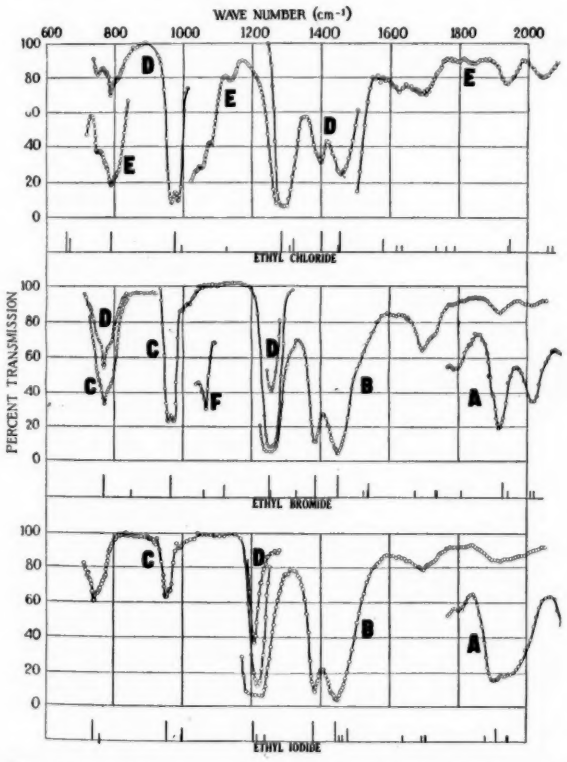


FIG. 1. Absorption spectra of ethyl halides 600 to 2000 cm^{-1}.

Any differences in positions of the bands observed here and those obtained from Raman data are probably due to the differences in the intensities of the fine structure components, causing a difference in the point of maximum intensity of the envelope as measured by the two methods. The positions of the fundamentals in absorption measurements may, in some cases, be affected by the proximity of other absorption bands.

Interpretation of Spectra

The intensities of absorption at the different bands is indicated roughly by the percent transmission plotted as ordinates in Figs. 1 and 2. The intense absorption in certain bands, even for very small quantities of absorbing material, leads to the conclusion that these bands are fundamentals, involving displacements of the atoms only to the first excited quantum state. The displacements to higher quantum states and the combination between two sets of quantum states are less probable; and, consequently, the harmonics and the combination frequencies show less intense absorption.

In the region investigated there are six intense absorption bands for each compound corresponding to fundamental frequencies. Two additional fundamentals of lower frequency, fully established from Raman spectra, give a total of eight experimentally observed fundamentals out of a possible eighteen if the system is non-degenerate.

The harmonics and combinations of these fundamentals which play the most important part in the determination of the whole spectrum may be assumed to be of the types $2F_i$ and F_i+F_j. The following table gives the values of the wave numbers of the fundamentals and the combinations of these types for each of the three compounds studied. The values for the fundamentals are arbitrary values between those obtained in the present investigation by absorption measurements and those given by Raman data.

In Figs. 1 and 2 these calculated positions are indicated below each spectrum by 3-unit lines for fundamentals, by shorter 2-unit lines for first harmonics and by lines of 1-unit length for combinations. It will be observed that a region of intense absorption in the experimental curve is

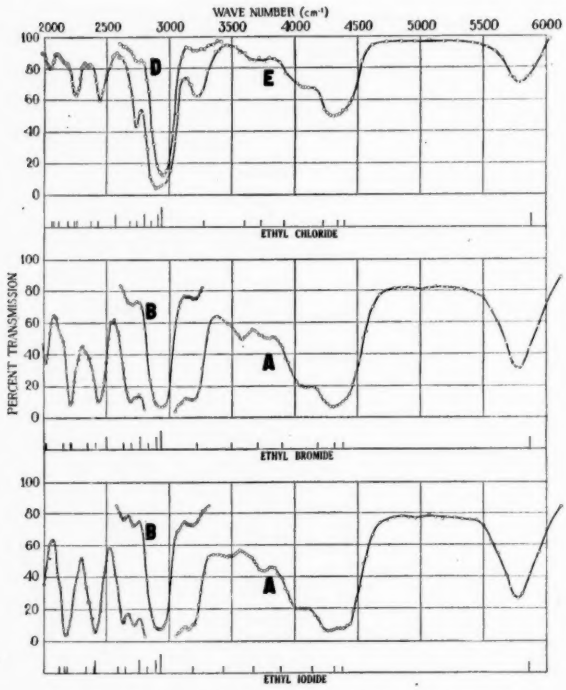


FIG. 2. Absorption spectra of ethyl halides 2000 to 6000 cm^{-1}.

indicated by the grouping of a number of calculated values, and that regions of high transmission are accompanied by a scarcity of calculated values. In fact the whole complex spectrum, experimentally determined, can be reconstructed with fair accuracy from these fundamentals and their first harmonics and combinations. The agreement cannot be exact because it is impossible to include all the factors involved. It is known, for example, that harmonics are not exact multiples of the fundamentals but that there are small correction terms.

Another cause for difference in calculated and observed spectra may be found in the fact that certain of the listed combinations may be very strong while others may be immeasurably weak, but it is not as yet possible to predict which are strong and which are weak.

The calculated positions do not represent all the possible absorption bands. There may be second or even higher harmonics, combinations of harmonics with fundamentals, etc., which are sufficiently strong to be factors in the observed spectra. Also there may be combinations of the type $F_i - F_j$ which are fairly strong. This will be particularly true when F_j is a low frequency fundamental, since a large fraction of these may be excited at room temperature.

Still another cause for the difference between the calculated and observed absorptions is the existence of weaker fundamentals. As an example of this, the Raman line at about 1065 cm^{-1} may be cited. Although this band did not appear in the transmission of the vapor cell, the curve F for 0.5 mm liquid ethyl bromide clearly shows a band in this region, perhaps a fundamental.

Approximate Motions Associated with the Frequencies

After selecting the most important fundamental frequencies from which the infrared spectrum is built, it becomes of interest to attribute to each a definite bond or type of vibration. Although such relations are quite speculative, there is now sufficient evidence to establish some of them with a fair degree of confidence.

The problem has been attacked by several investigators[6–11] using infrared and Raman measurements on a large number of organic compounds. In general, at least two different types of vibration seem to be well established: one a *stretching* vibration in which two atoms move back and forth essentially along a line joining their centers, and another, a *bending* vibration in which two atoms swing back and forth laterally with respect to a third atom or group of atoms. This previous work has been freely drawn upon in choosing some of the types of vibration given

[6] Coblentz, *Investigations of Infrared Spectra*, Carnegie Inst. Pubs. **35** (1905).

[7] Ellis, Phys. Rev. **27**, 298 (1926); **28**, 25 (1926).

[8] The work previous to 1931 is splendidly summarized by Kohlrausch, *Der Smekal-Raman Effekt*, Julius Springer, Berlin, 1931.

[9] Trans. Faraday Soc. **103** (1929). Symposium on Molecular Structure and Molecular Spectra Part III.

[10] Harkins and Bowers, Phys. Rev. [2], **38**, 1845 (1931).

[11] Harkins and Haun, J. Am. Chem. Soc. **54**, 3920 (1932).

TABLE I. *Calculated wave numbers of absorption bands.*

	Ethyl chloride	Ethyl bromide	Ethyl iodide
F_1	2940	2935	2930
F_2	1455	1450	1445
F_3	1400	1385	1380
F_4	1285	1250	1205
F_5	975	965	955
F_6	790	770	740
F_7	660	560	500
F_8	335	290	260
$2F_1$	5880	5870	5860
$2F_2$	2910	2900	2890
$2F_3$	2800	2770	2760
$2F_4$	2570	2500	2410
$2F_5$	1950	1930	1910
$2F_6$	1580	1540	1480
$2F_7$	1320	1120	1000
$2F_8$	670	580	520
F_1+F_2	4395	4385	4375
F_1+F_3	4340	4320	4310
F_1+F_4	4225	4185	4135
F_1+F_5	3915	3900	3885
F_1+F_6	3730	3705	3670
F_1+F_7	3600	3495	3430
F_1+F_8	3275	3225	3190
F_2+F_3	2855	2835	2825
F_2+F_4	2740	2700	2650
F_2+F_5	2430	2415	2400
F_2+F_6	2245	2220	2185
F_2+F_7	2115	2010	1945
F_2+F_8	1790	1740	1705
F_3+F_4	2685	2635	2585
F_3+F_5	2375	2350	2335
F_3+F_6	2190	2155	2120
F_3+F_7	2060	1945	1880
F_3+F_8	1735	1675	1640
F_4+F_5	2260	2215	2160
F_4+F_6	2075	2020	1945
F_4+F_7	1945	1810	1705
F_4+F_8	1620	1540	1465
F_5+F_6	1765	1735	1695
F_5+F_7	1635	1525	1455
F_5+F_8	1310	1255	1215
F_6+F_7	1450	1330	1240
F_6+F_8	1125	1060	1000
F_7+F_8	995	850	760

here, and Raman data and infrared absorption spectra of other compounds have been used to supplement the present absorption measurements on the ethyl halides.

It is a striking fact that the fundamental nature of the vibration between two atoms is affected only slightly by vibrations located in other parts of the molecule. Double bonds and other structural features do exert considerable influence, but they are not involved in the present discussion of the ethyl halides. A given vibration is affected only to a slight or negligible degree by a substitution of atoms in a part of the molecule removed from the immediate vibration. When, however, atoms of different weight are substituted in positions adjacent to the vibrating atoms the effect is more marked; and, if one of the atoms directly involved in the vibration is substituted, the change in frequency may be large. This fact has been used in choosing the types of vibration from the shifting of frequency caused by the chloride, bromide, iodide substitutions. The fundamental frequencies expressed in wave-numbers ($\tilde{\nu}$) have been given in Table I and are arbitrarily referred to as F_1, F_2, F_3, etc., starting with the highest frequency. The types of vibration which are believed to correspond to each of these fundamentals are pictured graphically in Fig. 3. Obviously these models represent simplified approximations and they are not to be taken literally.

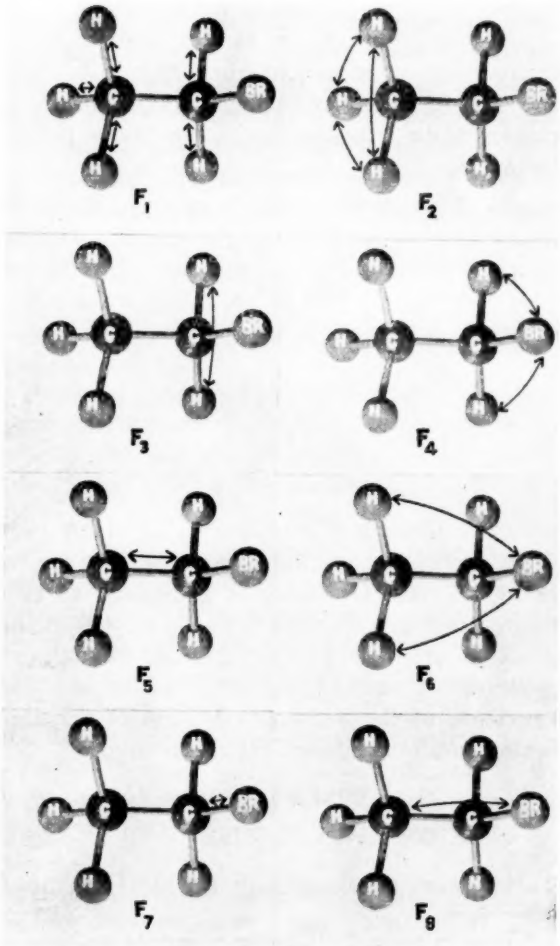


FIG. 3. Important features of the motions associated with the fundamental frequencies.

F_1. Wave-numbers ($\tilde{\nu}$) $C_2H_5Cl = 2940$, $C_2H_5Br = 2935$, $C_2H_5I = 2930$ cm^{-1}

Wave-lengths (λ) $C_2H_5Cl = 3.40$, $C_2H_5Br = 3.41$, $C_2H_5I = 3.42\mu$.

This frequency has long been associated with the carbon-hydrogen bond. Coblentz[6] in his classical examination of over a hundred organic compounds observed this intense band at about 3.4μ in every case where there was a simple linkage between carbon and hydrogen. In reality this band represents an average of 3 or 4 bands between 2850 and 3050 cm^{-1} in the case of the ethyl halides, but the average value is sufficient for the present purpose.

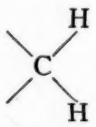
As shown in Fig. 3 this F_1 frequency is attributed to a stretching vibration of the carbon and hydrogen atoms toward and away from each other. This is perhaps the most common linkage in organic compounds and when, as is frequently the case, there are several such groups in a single molecule, the band becomes particularly prominent.

F_2. $\tilde{\nu} = 1455, 1450, 1445$ cm^{-1} *

$\lambda = 6.87, 6.90, 6.92\mu$

$\tilde{\nu}_{(\text{Raman})} = 1450, 1440, 1430$ cm^{-1}.

This frequency occurs only when the



group is present. For example, in chloroform ($CHCl_3$) F_1 is present but F_2 is missing. As shown in Fig. 3, this frequency is attributed to two hydrogen atoms swinging laterally at the side of a carbon atom. But as brought out in the next paragraph, it seems likely that this frequency is restricted to the bending vibration of pairs of hydrogen atoms in the CH_3 group only.

F_3. $\tilde{\nu} = 1400, 1385, 1380$ cm^{-1}

$\lambda = 7.14, 7.22, 7.25\mu$.

This frequency is very nearly the same as that of F_2, but it is distinguished from it by being slightly lower and particularly in being more easily influenced by the halogen. For this reason, as shown in Fig. 3, the vibration is attributed to the bending vibration of two hydrogen atoms not in the CH_3 group but in the $-CH_2Br$ group.

F_4. $\tilde{\nu} = 1290, 1255, 1210$ cm^{-1}

$\lambda = 7.75, 7.96, 8.26\mu$

$\tilde{\nu}_{(\text{Raman})} = 1276, 1240, 1197$ cm^{-1}.

The very large change produced in this frequency by substituting for bromine the lighter chlorine or the heavier iodine leads to the conclusion that the halogen atom is directly involved in the vibration. A bending vibration of halogen and hydrogen pivoting around the carbon atom is suggested for this vibration as shown in Fig. 3.

F_5. $\tilde{\nu} = 975, 965, 955$ cm^{-1}

$\lambda = 10.26, 10.36, 10.47\mu$

$\tilde{\nu}_{(\text{Raman})} = 966, 960, 951$ cm^{-1}.

The small change produced in this frequency by changing the halogen shows that the halogens are not directly involved. Furthermore, this frequency is found in ethane where no halogen is present. The fact that it is not found in methyl compounds shows that it is not due to a simple carbon-hydrogen vibration. All this evidence indicates that the F_5 frequency is due to a stretching vibration of the two carbon atoms along a line joining their centers as shown in Fig. 3.

This frequency seems to occur in all ethyl compounds except ethyl alcohol. This exception may be due to the fact that the two end groups, the OH and the CH_3 groups, having nearly equal physical properties, tend to interact and produce types of vibration in which the local features give way to features involving the whole molecule.

F_6. $\tilde{\nu} = 790, 770, 740$ cm^{-1}

$\lambda = 12.65, 13.00, 13.5\mu$.

The F_6 frequency, like the F_4 frequency, changes so markedly with substitution of the different halogens that vibration of the halogen atom must be directly involved. This frequency is not found in methyl halides. Accordingly, a bending vibration involving the halogen atom and a hydrogen atom on the second carbon atom is tentatively proposed as shown in Fig. 3.

* These values in the following paragraphs are given in the order ethyl chloride, ethyl bromide, and ethyl iodide respectively, as indicated after F_1.

F_7. $\tilde{\nu}_{(\text{Raman})} = 655, 560, 500\ \text{cm}^{-1}$
$\lambda = 15.3, 17.8, 20.0\mu$.

This frequency is beyond the range of the spectrometer because it falls in the region where rocksalt is no longer transparent. It is taken from Raman data alone. Since this frequency is changed so much by substitution of the halogen, it must be connected directly with a vibration of the halogen; and the low frequency suggests that heavy atoms may be involved. Harkins and Bowers[10] and others have suggested that this frequency is due to a stretching vibration of the carbon and halogen atoms.

This frequency changes only slightly (less than 10 percent) in going from the methyl halides to the ethyl halides and remains practically constant for the normal halides of the higher members of the series. The fact that the addition of more carbon atoms has so little effect on the frequency may be taken to strengthen the view that the motion is essentially along a line joining the halogen and the carbon atom to which it is bound, as shown in Fig. 3.

F_8. $\tilde{\nu}_{(\text{Raman})} = 335, 290, 260\ \text{cm}^{-1}$
$\lambda = 29.9, 34.5, 38.5\mu$.

This low frequency revealed by Raman data is likewise beyond the range which can be measured with the spectrometer used in the present investigation. The large change produced by the substitution of the different halogens indicates that the halogen is one of the vibrating atoms, and the low frequency suggests a bending vibration with heavy atoms involved. This frequency does not occur in methyl compounds, but it does occur in various ethyl compounds in which a halogen, OH or SH group is involved. As shown in Fig. 3, a bending motion is suggested in which the halogen and the second carbon atom oscillate at the side of the CH_2 group.

As pointed out before, there are no doubt other fundamental frequencies which have missed detection because they are considerably weaker than the ones described here and designated as F_1 to F_8. For example, a Raman line is found at 1070, 1065 and 1050 cm^{-1}. This was missed in the first absorption measurements, but, after a special search, using different absorbing thickness, it became plainly evident in ethyl bromide at 1065 cm^{-1}. This frequency shows little change with the halogen substitutions and it is not found in the methyl halides. It may be attributed, tentatively, to a bending vibration between a hydrogen and the second carbon atom. It is not shown in Fig. 3. If this is a correct interpretation, it seems strange that the line is not more intense because there should be opportunity for several different atoms to contribute to this frequency.

Theoretical Discussion

Each type of vibration has been represented as involving only two or three atoms, but, when a molecule is exposed to continuous radiation in the infrared region, all the fundamental frequencies and those corresponding to the various harmonics and combinations are absorbed, so that several different vibrations may be occurring simultaneously. Likewise, when the molecule becomes activated by collision or by other agency, several of these vibrations may be brought into play at the same time.

It is hoped that a knowledge of these types of vibration, such as those depicted in Fig. 3, will be helpful, eventually, in predicting ways in which chemical changes can take place. Some of them coincide with concepts of organic chemistry suggested long before there was physical evidence for their existence.

Andrews[12] has been quite successful in reproducing the fundamental frequencies of the Raman spectra with mechanical models excited to small amplitudes, a fact which indicates that the mechanical models and classical mechanics do give an approximate representation of the vibrational structure and behavior of the molecules. However, amplitudes as small as those employed by Andrews are connected with the chemical reactivity only in an indirect manner.

If, as is suggested by Rice and Ramsperger[13] and others,[14] molecules which decompose unimolecularly do so when a sufficient amount of energy becomes localized in a particular bond or type of vibration, it would seem logical that the

[12] Andrews, Ind. Eng. Chem. **23**, 1232 (1931).

[13] Rice and Ramsperger, J. Am. Chem. Soc. **49**, 1617 (1927).

[14] Kassel, *Kinetics of Homogeneous Gas Reactions*, Chapters V and X, Chemical Catalog Co., New York, 1932.

particular vibration should be a bending vibration rather than a stretching one, since the bending motion will bring close together certain parts of the molecule which may be able to interact with each other. A rearrangement to give new molecules may result. For example, it has been established[15] that ethyl bromide decomposes according to the equation $C_2H_5Br = C_2H_4 + HBr$ and that the reaction is definitely unimolecular.

It follows, therefore, that this decomposition would more likely take place by the oscillation of a hydrogen and a bromine atom toward each other transversely than by a mechanism wherein the first step is dissociation into a radical and a free atom by a stretching vibration such as F_1 or F_7. Such a disruption into free atoms should require considerably more energy. Furthermore, the absence of detectable amounts of side products such as higher hydrocarbons and various bromine derivatives supports the view that the dissociation involves a single molecule rather than an associated complex. The rupture could take place in the same manner, however, even if a complex unit of two or more molecules were involved.

The types of vibrations suggested for F_6 or F_8 and shown in Fig. 3 would both lead to a close approach of an atom of bromine and an atom of hydrogen from the second carbon atom, and, with sufficient amplitude, this might lead to a rearrangement of the forces within the molecule and result in the formation of ethylene and hydrogen bromide.

If chemical rupture of the molecule can be brought about by the proper type of vibration between the atoms, it might seem at first sight that infrared radiation should be photochemically active, but the experimental facts, thus far, show that infrared radiation is photochemically inactive.[16, 17] The fundamental frequencies described in the present communication correspond to displacement of the atoms only to the first quantum state, and the first harmonics involve displacements to the second quantum state. These displacements fall far short of giving sufficient amplitude of vibration to bring about the chemical dissociation already described.

Speaking specifically of ethyl bromide, the energy of activation calculated from the temperature coefficient of the thermal dissociation rate is 54,800 calories per mol.[15] This energy of activation would correspond to a wave number of 19,300 cm^{-1} (in the green part of the visible spectrum) whereas the wave number of the fundamental frequency F_6 is only 770. In other words, it would take at least the 25th harmonic (perhaps the 30th or 40th with due allowance for an anharmonic factor) to provide sufficient energy to disrupt the molecule of ethyl bromide, assuming such a mechanism of disruption for both the thermal and the photochemical dissociations. But, as has been shown, the first harmonics are much less intense than the fundamental, and the second harmonics are still very much weaker. The absorption of any of the higher harmonics in the region of the 25th harmonic would be utterly negligible. For example, Ellis[18] found it necessary to use a tube of liquid chloroform 4.5 meters long in order to detect even the sixth harmonic of the carbon-hydrogen fundamental, designated here as F_1.

In other words, no matter how great the radiation density, the fundamental frequencies cannot decompose the molecules because the energy of the quantum is not large enough; and a harmonic having sufficiently high frequency to give decomposition is not absorbed. Consequently it is unlikely that a molecule can be disrupted by radiation which acts only in causing the atoms to oscillate. The critical vibration of large amplitude (high-quantum states) leading to chemical dissociation must be effected in other ways,—by violent collisions from thermal agitation or by electronic excitation, for example.

Although it has been shown that the fundamental frequencies of given types of vibration are relatively independent of the nature of the remainder of the molecule, it is by no means implied that the energy terms of a given type are independent of the degree of excitation of the various other types of vibration when the amplitude is large and the motion is anharmonic. Indeed, it would seem more in keeping with the

[15] Vernon and Daniels, J. Am. Chem. Soc., in press.

[16] Daniels, J. Am. Chem. Soc. **48**, 607 (1926); Chem. Rev. **5**, 54–56 (1928).

[17] Taylor, J. Am. Chem. Soc. **48**, 577 (1926).

[18] Ellis, Phys. Rev. **32**, 906 (1928).

modern view of the energy relationships of such systems to believe that there might be considerable influence exerted between the highly excited states. Thus, although a certain amount of energy localized in a given type of vibration may be sufficient to cause the decomposition of a molecule, it may be true that a smaller amount of energy in that type, when accompanied by additional energy in certain other types, will cause the decomposition to take place. Since little is known of the vibrational energy states of complex molecules, or the nature of the interchange of energy between the different types of vibration, a quantitative treatment of the problem is not possible at this time.

In closing the authors wish again to emphasize the fact that the speculations based on their experimental facts are tentative and incomplete. Exact analysis of the systems studied may alter the interpretation given here, but such analysis is as yet impossible. Chemists find it helpful to try to connect physical and chemical properties with molecular models, although physicists often object to such models because they are inadequate in more quantitative fields.

The present hypotheses regarding atomic motions in the molecule are offered in the hope that further discussion and additional experiments may justify the incomplete picture as useful until a more complete one is possible.

The slight differences in the spectra of the structurally similar ethyl halides have been helpful in interpreting the spectra. Likewise, a comparison of the dissociation rate of ethyl iodide and chloride with that of the bromide may be helpful in the study of kinetics. These systems then seem particularly favorable for an extended study of the relation between molecular structure and chemical reaction.

The authors are glad to acknowledge the generous support of the Wisconsin Alumni Research Foundation during a part of this investigation.

The Normal State of the Helium Molecule-Ions He_2^+ and He_2^{++}

LINUS PAULING, *Gates Chemical Laboratory, California Institute of Technology*

(Received October 31, 1932)

With the use of wave functions constructed from hydrogen-like single-electron functions with an effective nuclear charge Z, the application of the variation method of treating the wave equation for the normal state of He_2^+, involving a three-electron bond, leads to the values $Z=1.833$, $r_0=1.085$A, $D_e=2.47$ v.e., and $\omega_0=$approximately 1950 cm^{-1}. The experimentally determined values (from the He_2 spectrum) are $r_0=1.090$A, $D_e=2.5$ v.e., and $\omega_{\frac{1}{2}}=1628$ cm^{-1}. A similar discussion of He_2^{++}, with a covalent-plus-ionic wave function, shows that the energy curve has a minimum at $r_0=0.75$A, $\omega_0=$approximately 3200 cm^{-1}, with a maximum 1.4 v.e. higher at about 1.1A. This configuration could act as the core for excited states of He_2^+ and doubly-excited states of He_2, some of which would be capable of existence with either one of two moments of inertia, one corresponding to $r_0=0.75$A and the other to about the same values of r_0 as for the analogous states in excited H_2^+ or doubly-excited H_2.

THE NORMAL STATE OF He_2^+

IT has been pointed out[1] that the degeneracy represented by the two symbols He: $\cdot He^+$ and $He\cdot^+$: He, in which each dot represents a $1s$ electron, would lead to attraction and the formation of a bond between the two atoms, which may be called a three-electron bond; and it was suggested that as a rule such a bond should be about as strong as a one-electron bond, such as that in H_2^+, and weaker than an electron-pair bond, as in H_2. The following wave-mechanical treatment of the ion He_2^+ was made to verify (or disprove) these statements. The treatment used is closely analogous to that applied to the hydrogen molecule by Heitler and London,[2] Sugiura,[3] and Wang,[4] and to the hydrogen molecule-ion by Pauling[5] and Finkelstein and Horowitz.[6] In these cases the equilibrium internuclear distances obtained agree with experiment to within a few percent, and the dissociation energies to within about 25 percent; similar agreement can hence be expected for the helium molecule-ion calculations. The integrals which occur in the calculations are all well known, being given, for example, in reference 5, so that it has seemed unnecessary to give explicit expressions for the energy integrals discussed in the following pages.

With $a_0=0.529$A, e, and $e^2/a_0=27.06$ v.e. as units of length, electrical charge, and energy, Schrödinger's equation becomes $\nabla^2\psi+2(W-V)\psi=0$, with $V=\Sigma z_i z_j/r_{ij}$, in which $z=-1$ for an electron, 2 for a helium nucleus, and the summation includes each pair of charges once. The value of the energy integral $\int\Psi^*H\Psi d\tau/\int\Psi^*\Psi d\tau$, with $H=-\frac{1}{2}\nabla^2+V$, for an arbitrary function Ψ is known to be greater than or equal to the energy W_0 of the lowest state of the system.

A simple wave function for the system of two helium nuclei A and B and three electrons 1, 2, and 3 can be constructed of hydrogen-like $1s$ functions $\psi=Z^{3/2}\pi^{-1/2}e^{-\xi/2}$, with $\xi=2Zr_A$, and a similar expression in r_B for φ, by assuming that each electron interacts only with one nucleus. The two antisymmetric functions Ψ_{I} and Ψ_{II}, represented by the scheme

	ψ	φ	Σm_s		
I	$+-$	$+$	$+\frac{1}{2}$	He :	$\cdot He^+$
II	$+$	$+-$	$+\frac{1}{2}$	He $.^+$	: He

can then be constructed by Slater's method,[7] as well as two other functions with $\Sigma m_s=-\frac{1}{2}$ which do not combine with these, and which give rise to the other components of the doublet levels. Because of the identity of the nuclei the nuclear-symmetric and nuclear-antisymmetric functions $\Psi_S=\Psi_{\text{I}}+\Psi_{\text{II}}$ and $\Psi_A=\Psi_{\text{I}}-\Psi_{\text{II}}$ provide better

[1] L. Pauling, J. Am. Chem. Soc. **53**, 3225 (1931).

[2] W. Heitler and F. London, Zeits. f. Physik **44**, 455 (1927).

[3] Y. Sugiura, Zeits. f. Physik **45**, 484 (1927).

[4] S. C. Wang, Phys. Rev. **31**, 579 (1928).

[5] Linus Pauling, Chem. Rev. **5**, 173 (1928).

[6] B. N. Finkelstein and G. E. Horowitz, Zeits. f. Physik **48**, 118 (1928).

[7] J. C. Slater, Phys. Rev. **38**, 1109 (1931).

approximations to the correct wave functions than do Ψ_{I} and Ψ_{II} individually. The energy integral for these functions is

$$E=(H_{\text{I I}}\pm H_{\text{I II}})/(d_{\text{I I}}\pm d_{\text{I II}}),$$

with

$$H_{\text{I I}}=\int\psi(1)\psi(2)\varphi(3)H\psi(1)\psi(2)\varphi(3)d\tau - \int\psi(1)\psi(2)\varphi(3)H\varphi(1)\psi(2)\psi(3)d\tau$$

$$H_{\text{I II}}=\int\psi(1)\psi(2)\varphi(3)H\psi(1)\varphi(2)\varphi(3)d\tau - \int\psi(1)\psi(2)\varphi(3)H\varphi(1)\varphi(2)\psi(3)d\tau,$$

and with similar expressions for the d's, with 1 in place of H.

On placing Z equal to 2, there are obtained the curves shown in Fig. 1 representing the energy

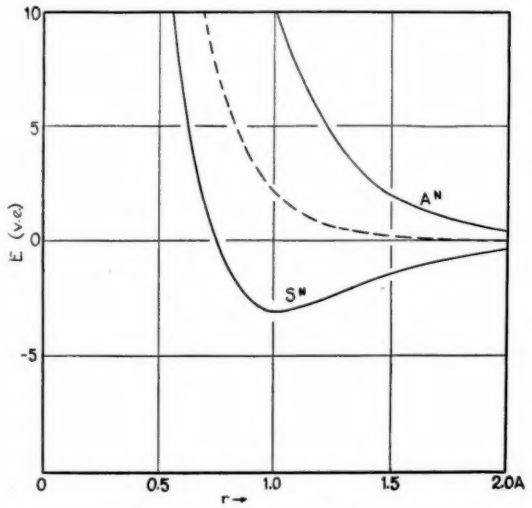


FIG. 1. Energy curves for attractive and repulsive states of He_2^+. The dashed curve corresponds to a non-existent state, resonance between He : $\cdot He^+$ and $He\cdot^+$: He being excluded.

as a function of r, the internuclear distance, the energy at $r=\infty$ being taken as zero. As in Heitler and London's treatment of the interaction of two normal hydrogen atoms, the nuclear-antisymmetric state does not lead to the formation of a stable molecule, the forces between the atoms being repulsive at all distances. The nuclear-symmetric state gives a potential function with a pronounced minimum at $r_0=1.01$A, with a dissociation energy of 2.9 v.e.

In Fig. 1 the dashed curve represents the energy $H_{\text{I I}}/d_{\text{I I}}$, corresponding to the wave function Ψ_{I} or Ψ_{II} alone. Comparison of this curve with that for $\Psi_{\text{I}}+\Psi_{\text{II}}$ provides justification for the statement that the three-electron bond results from resonance of the system between the two degenerate states represented by the symbols He : $\cdot He^+$ and $He\cdot^+$: He. It is evident that for unlike atoms for which the energy difference of the states $A:\cdot B$ and $A.:B$ is greater than the resonance energy between these two states, the correct wave functions approximate Ψ_{I} and Ψ_{II}, and do not lead to the formation of a stable three-electron bond.

A more accurate treatment of He_2^+ results on minimizing the energy with respect to the effective nuclear charge Z. On introducing the variable $\rho=Zr$, the process of minimizing with respect to Z can be carried out analytically, as pointed out by Wang,[4] with subsequent determination of the minimum relative to ρ by numerical calculation. This treatment leads to $Z=1.833$, with the equilibrium internuclear distance $r_0=1.085$A. The dissociation energy to $He+He^+$ (energy -9.630 Rhc, for $Z=43/24$) is found to be $D_e=2.47$ v.e., and the vibrational frequency approximately 1950 cm^{-1}, obtained from values of the energy calculated in the neighborhood of r_0 by holding Z constant. The experimental values of these quantities,[8] from measurements of the spectrum of He_2 in states consisting of a normal He_2^+ ion and an outer electron, are $r_0=1.090$A, $D_e=2.5$ v.e., and $\omega_{1/2}=1628$ cm^{-1}, in excellent agreement with the theoretical values. The dissociation energy is nearly equal to that for H_2^+, $D_e=2.76$ v.e., as expected.

Although the variation treatment leads to an energy value for the system greater than or equal to the energy of the lowest state of the system, the calculated value of D_e given above is not a lower limit to the true value, inasmuch as an approximate wave function has been used both for $r=r_0$ and $r=\infty$, and it is not known at which point the error is greater.

A closer approximation to the wave function could be obtained by using different values of Z for He : and $\cdot He^+$; because of the complexity of the calculations and the small expected improvement, this treatment has not been carried out.

[8] W. Weizel, *Bandenspektren*, Akad. Verlagsges. m.b.h. Leipzig, **1931**, pp. 255, 270.

The Normal State of He_2^{++} and the Spectrum of He_2^+

The wave functions for He_2^{++} which can be constructed from 1*s* hydrogen-like functions are, as for H_2 also, the following:

	ψ	φ		
I	+	−	H .	. H
II	−	+	H .	. H
III	+−		H:⁻	H^+
IV		+−	H^+	:H^-

From these we obtain the nuclear-symmetric functions $(\Psi_I-\Psi_{II})+\alpha(\Psi_{III}+\Psi_{IV})$ and $(\Psi_I-\Psi_{II})-\beta(\Psi_{III}+\Psi_{IV})$, and similar nuclear-antisymmetric functions. The first function provides a close approximation to the wave function for normal H_2, the ionic parameter α being equal[9] to 0.256, with $Z=1.193$ and $r_0=0.750$A. On minimizing the energy integral for this function for He_2^{++} with respect to α, Z, and ρ, the values $\alpha=0.435$, $Z=2.124$, and $r_0=0.75$A are obtained. The course of the energy as a function of r, calculated for these values of α and Z, is shown in Fig. 2. It is seen that at large distances the two

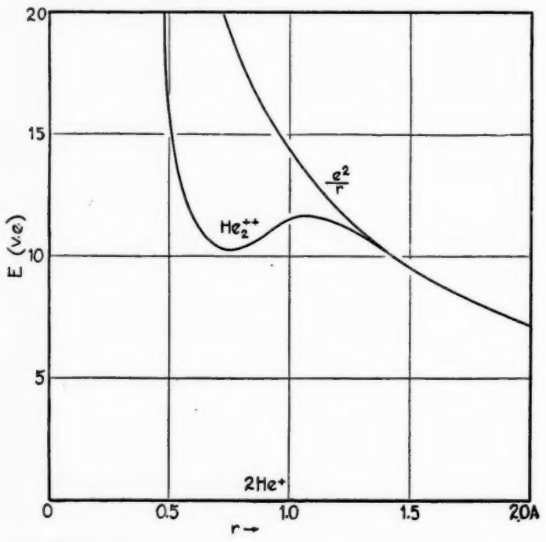


FIG. 2. The energy curve for normal He_2^{++}.

He^+ ions repel each other with the force e^2/r^2; at about 1.3A the resonance interaction of the electrons becomes important, causing the force to become attractive at about 1.1A, and leading to the formation of a molecule which is probably sufficiently metastable to give rise to a band spectrum. The predicted constants for this state are $r_0=0.75$A, $D=1.4$ v.e. (distance from minimum to maximum), and $\omega_0=3200$ cm^{-1}, with four vibrational levels occurring, the fourth (and perhaps the others also) probably showing pronounced predissociation characteristics. There are no experimental data existent with which to compare these values. However, excited states of He_2^+ consisting of this state of He_2^{++} with an outer electron, and having approximately these values of r_0, D, and ω_0, should give rise to well-defined He_2^+ bands, bearing approximately the same relation to the He_2 bands that the He^+ spectrum does to the H spectrum; it is hoped that these bands will be observed by the experimental spectroscopists.

It is interesting to note that of these states of He_2^+ about one-half should be capable of existence with either of two moments of inertia; that is, the electronic energy curves should show two minima. At $r=0.75$A the two He^+ ions are held together by an electron-pair bond formed by the two atom-cores, the outer electron being roughly hydrogen-like, and contributing little to the bond. This gives rise to states of He_2^+ which resemble closely in their values of r_0 and ω_0 the normal state of He_2^{++} just discussed, in the same way that many known states of He_2 and of H_2 resemble the normal states of He_2^+ and of H_2^+, respectively. At larger distances, of 3 or 4A, the He^+ ions simulate protons with regard to their interaction both with each other and with an outer electron; and if the outer electron is in a nuclear-symmetric state, it will hold them together in the same way that the protons in excited states of H_2^+ are held together by the excited electron. This statement can be made without carrying out the calculation of the energy curves, inasmuch as previous calculations for atoms with one electron in a non-penetrating orbit outside of a *K*-shell, such as Li $1s^22p$, He $1s2p$, etc., have shown that the interaction of the outer and inner electrons has very little influence in changing the wave function and energy value from those corresponding to complete screening,

[9] S. Weinbaum, private communication; J. C. Slater, Phys. Rev. **35**, 509 (1930).

and the calculations given above for $He^+ + He^+$ show that at these internuclear distances the interaction of the two atom-cores is essentially equal to that of two protons. The energy corresponding to resonance between the two states $\cdot He^* \cdot \; He \cdot^+$ and $\cdot He^+ \; \cdot He \cdot^*$ will accordingly cause the potential curves for various excited states to show minima, corresponding to stable states of $\cdot He \cdot He \cdot^+$, with a one-electron bond formed by the excited electron. These states will be very closely similar to the excited states of H_2^+, but with quadrupled moments of inertia. States of He_2 with two excited electrons would in some cases also show two minima, one at $r = 0.75$A, and one at some larger value, approximately equal to that for the corresponding state of doubly-excited H_2.

Certain relations between equilibrium distances for bonds formed by K electrons may be pointed out. The electron-pair bond in He_2^{++} leads to the same value for r_0 (0.75A) as for H_2 (0.750A). The three-electron bond in He_2^+ leads to $r_0 = 1.09$A, nearly equal to the value $r_0 = 1.06$A for the one-electron bond in H_2^+. The oscillational frequencies in He_2^{++} and He_2^+ are approximately three-quarters of those for H_2 and H_2^+, respectively.

I am indebted to Mr. Sidney Weinbaum for carrying out many of the calculations involved in this work.

The Dipole Moment of Nitric Oxide

C. P. SMYTH AND K. B. MCALPINE, *Princeton University*

(Received November 1, 1932)

The dielectric constant of nitric oxide is measured over a wide range of temperature and used to calculate the dipole moment of the molecule, which is found to be less than 0.1×10^{-18}, and so small as to be indistinguishable from zero.

BECAUSE of the importance of nitric oxide as one of the simple and frequently discussed molecules, it has seemed desirable to obtain an accurate value for its dipole moment.

Experimental Method

The dielectric constant of the gas was measured with an apparatus and method to be described elsewhere. Since, at the pressures and temperatures here used, the deviation of nitric oxide from the ideal gas laws is small in comparison with the experimental error, the determinations at each temperature were made at approximately the same pressure, the pressures used being such as would maintain the observed dielectric constant at approximately the same value and thus restrict the capacity readings to the same range on the precision condenser. The relative accuracy of the determinations of the small dielectric constant values was, in this way, increased. The vacuum capacity of the apparatus was determined after each measurement with gas in the condenser.

Preparation of Nitric Oxide

The nitric oxide was prepared by the method used by Noyes,[1] concentrated sulfuric acid being dropped upon sodium nitrite covered with two or three times its weight of water. The gas evolved was passed through concentrated sulfuric acid and dilute sodium hydroxide solution in spiral wash bottles, through calcium chloride and phosphorus pentoxide tubes, then very slowly through a coil surrounded by a mush of petroleum ether maintained at about -130°C to remove less volatile impurities, in particular, any other oxides of nitrogen not previously absorbed. Finally, it was condensed in a trap surrounded by liquid air and subjected to fractionation. The liquid obtained in the trap had a faint blue color which could not be removed by repeated passage through the coil at -130°. The trace of higher oxides indicated by this color was too small to affect the results.

[1] W. A. Noyes, J. Am. Chem. Soc. **47**, 2170 (1925).

Experimental Results

From each measurement of the dielectric constant ϵ, the polarization was calculated as $P=[(\epsilon-1)/(\epsilon+2)]V$, where V is the molar volume. In Table I, the first column gives the absolute temperature at which each run or

TABLE I. *Experimental data.*

T, °K	p(mm)	P	Mean	T, °K	p(mm)	P	Mean
235.2	579.4	4.83		355.9	816.6	4.85	
(7)	576.4	4.79		(8)	857.5	4.81	
	565.4	4.84			853.1	4.79	
	579.1	4.80			849.7	4.88	
	578.4	4.78			852.7	4.78	4.82
	581.0	4.80	4.81				
				384.5	931.7	4.86	
266.5	678.8	4.87		(3)	949.9	4.85	
(6)	686.3	4.85			949.3	4.84	
	673.9	4.85			943.0	4.81	
	682.2	4.88			948.3	4.81	
	669.6	4.90	4.87		947.4	4.80	4.83
299.3	752.2	4.88		421.9	1021.0	4.84	
(1)	753.0	4.91		(4)	1028.6	4.82	
	752.5	4.89			1031.9	4.84	
	755.4	4.85			1034.2	4.79	
	753.3	4.85			1025.4	4.80	
	751.0	4.86			1028.7	4.78	4.81
	753.5	4.86					
	750.4	4.85	4.87	477.0	1103.6	4.76	
				(5)	1118.8	4.78	
335.4	790.9	4.93			1115.1	4.79	
(2)	790.5	4.89			1149.6	4.78	
	794.4	4.89			1154.6	4.83	
	797.8	4.92			1147.5	4.82	
	817.3	4.88			1146.6	4.81	
	814.6	4.88			1155.2	4.82	4.80
	829.0	4.94	4.90				

$a=4.75$, $b=28$, $MR_\infty=4.31$,
$P_A=0.44$, $\mu=0.0_7\times10^{-18}$.

series of measurements was made and, under each temperature, the number of the run in parentheses. The second column gives in order the pressures at which the measurements were made, the third column the polarization calculated from the dielectric constant, and the fourth column the mean of the polarization values at each temperature, the order being repeated in the second half of the table. At the bottom of the table are the values of the constants of the Debye equation, $P=a+b/T$, obtained from the mean values of P by the method of least squares. The value of the atomic polarization was calculated as $P_A=a-MR_\infty$, the molar refraction for infinite wave-length, MR_∞, being obtained by extrapolation from values in *International Critical Tables*. The electric moment was calculated from b as $\mu=0.0127\times10^{-18}(b^{\frac{1}{2}})$.

Discussion of Results

The polarization values in Table I pass through a maximum which is 2 percent higher than the values found at the highest and lowest temperatures. Although this 2 percent difference is larger than the probable error as estimated for the apparatus and as evidenced by the agreement between the individual measurements at any one temperature, it is too small to have any definite significance. There is obviously no regular falling off of the polarization with rising temperature as required by the Debye equation for a substance with a dipole moment in the molecule. The value of b is too small to have real significance, which means that the value given for the moment is so small as to be indistinguishable from zero. This does not mean, however, that the moment is necessarily 0, but, rather, that it is less than 0.1×10^{-18}, distinctly smaller than the value, 0.2×10^{-18}, used by Huber[2] in the investigation of the possibility of a magneto-electric directive effect, and obtained from an unpublished dielectric constant value determined by Sänger and regarded by him as uncertain.

As the carbon monoxide molecule has a greater difference between its two nuclear charges than has nitric oxide and yet has a moment of only 0.11×10^{-18},[3] it is not surprising to find so small a moment in nitric oxide. It is also in harmony with the small or zero moment found for the seemingly unsymmetrical molecule of nitrous oxide.[3] Evidently, the odd number of electrons in the nitric oxide molecule, which gives rise to paramagnetism, causes nothing out of the way in the dipole moment.

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[2] A. Huber, Phys. Zeits. **27**, 619 (1926).

[3] Smyth, *Dielectric Constant and Molecular Structure*, New York, The Chemical Catalog Company, Inc., (1931) p. 192.

The Symmetry of the Benzene Molecule*

V. Deitz and D. H. Andrews, *Chemistry Laboratory, Johns Hopkins University*

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The melting points of various isomeric organic compounds indicate that molecular symmetry has an important effect on physical properties. With R. H. Fowler's statistical treatment of the crystal state, the symmetry number has been calculated for benzene and cyclohexene. The data employed are the vapor pressure, the heat capacity of the crystal, the heat capacity of the vapor as calculated from Raman spectra, the heat of sublimation and the moments of inertia. According to this calculation the symmetry number for benzene has the value 6 ± 0.5 indicating that the molecule is not plane. The symmetry number for cyclohexene is 2 ± 0.2 as is to be expected.

RECENT developments in statistical mechanics and quantum mechanics have made clear the importance of the symmetry of the molecule in various physical and chemical processes. This property must be ranked as of equal influence with mass and energy in many instances where the process in question involves molecular orientation. For example, one finds great differences among the melting points of certain series of organic compounds which have approximately the same mass, thermal energy, and differ only in shape or symmetry. One of the most striking cases is the series of hydrogenated benzene derivatives: benzene, cyclohexadiene, cyclohexene, and cyclohexane.

We may define the symmetry of these compounds in the manner of Ehrenfest and Trkal[1] who were the first to point out the role of symmetry in statistical mechanics. These authors assign to each type of molecule a symmetry number which is defined as the number of equivalent positions which the molecule may assume when it executes all possible rotations in space. Thus with benzene, if we assume a flat molecule, we may rotate the ring in its own plane and find six equivalent positions, and by turning the ring over six more, giving a total symmetry number of twelve. The same is true of cyclohexane. Ordinary cyclohexadiene and cyclohexene have both a symmetry number of two. Cyclohexadiene with the double bonds in the 1–2 and 4–5 position has a symmetry number of four. As is shown in Table I, the melting points of these compounds vary over a hundred degree range and appear to be related to the molecular symmetry. Thus, the removal of the first double bond presumably lowers the symmetry of the ring from 12 to 2 and we get a drop in melting point from 5.5 to -95°C. The removal of still another double bond causes no change in symmetry and little in melting point. The last step, however, which restores the symmetry to something like that of benzene, raises the melting point to within a tenth of a degree of its original value.

We can form a qualitative idea of the reason for this influence of symmetry on melting point by observing the distinction between the processes of liquid forming from crystal and of crystal forming from liquid. The melting point is the temperature at which these two processes are in equilibrium. In the first case, crystal to liquid, the factors which fix the rate are the mass, thermal energy, and intermolecular force. If these are the same, a symmetrical or unsymmetrical molecule have both the same chance of escaping from the crystal.

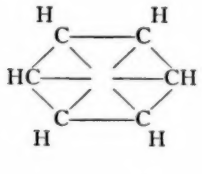
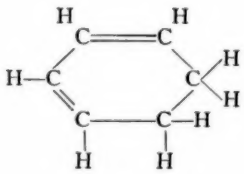
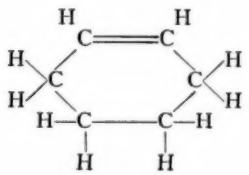
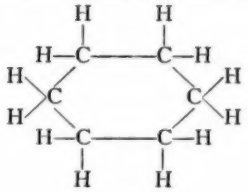
In the reverse process, however, if we consider a symmetrical and an unsymmetrical molecule under exactly the same conditions, the former has the greater chance of orienting itself properly to fit into the crystal lattice. Freezing therefore takes place at a higher temperature. This rule is verified qualitatively in dozens of series of organic isomers.

As contrasted with the melting points, the boiling points of this series lie within a very narrow range of temperature. The processes of going

* From the dissertation submitted by V. Deitz to the Johns Hopkins University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[1] Ehrenfest and Trkal, Proc. Roy. Soc. (Amsterdam) **23**, 162 (1920).

TABLE I.

				
	C_6H_6 Benzene	C_6H_8 Cyclohexadiene	C_6H_{10} Cyclohexene	C_6H_{12} Cyclohexane
M.P.	+5.48°C	−95.°C	−103.7°C	+6.4°C
B.P.	+80.2°	+81.°	+81.6°	+80.0°
Mol. Wght.	78.04	80.06	82.08	84.10

from liquid to vapor and from vapor to liquid do not, of course, involve molecular orientation, so it is to be expected that molecular symmetry will have little influence. The fact that boiling points do lie so close together is evidence that the other factors such as thermal energy and intermolecular force vary only slightly throughout the series, at least in the region of the boiling point.

These qualitative evidences of the influence of symmetry on melting point made it appear worth while to look for a really quantitative measure of the effect of symmetry on physical properties in general. For this purpose the vapor pressures of crystals appear more promising than their melting points. As may be seen from the discussion which follows, symmetry may be regarded as influencing the behavior of a molecule through its effect on the entropy of the molecule. To determine the absolute entropy of the vapor state we may calculate the change in entropy as the system proceeds by various paths from a state of zero entropy, the crystal at absolute zero, to the vapor state. Thus it may pass from the ordered crystal phase to the chaotic vapor phase either directly by sublimation, or by melting to liquid and vaporization. Consequently one may infer that symmetry will play a part in determining the absolute entropy and therefore the vapor pressure of either crystal or liquid.

The first step in solving this problem is to set up the vapor pressure equation for a crystal, using the various terms, found in statistical mechanics, one of which involves a factor directly measuring the molecular symmetry. Fowler[2] has given the most thorough discussion of the background of statistical mechanics needed for this problem and we shall use his treatment as the basis for discussion.

We take as a starting point the following equation (Fowler, Eq. (436)) which may be derived on the basis of classical thermodynamics:

$$\ln p = -\frac{\lambda_0}{RT} + \int_0^T \frac{dT}{RT^2} \int_0^T (C_{vap.} - C_{sol.})dT + i, \quad (1)$$

where λ_0 is the molal heat of sublimation at $T=O$, and i is a chemical constant defined by this equation. $C_{vap.}$ and $C_{sol.}$ are the heat capacities per mole of the vapor and crystal at constant pressure.

We now let $(C_p)_0$ represent the constant part of $C_{vap.}$ i.e., the part which has already attained its classical value, and we let $(C_p)_1$ represent the variable part of $C_{vap.}$ Eq. (1) may then be put in the form

$$\ln p = -\frac{\lambda_0}{RT} + \frac{(C_p)_0}{R} \ln T + \int_0^T \frac{dT}{RT^2} \int_0^T \{(C_p)_1 - C_{sol.}\}dT + i. \quad (2)$$

It is possible to express statistically rather than thermodynamically the part of this which depends on the variable specific heats. Using the partition functions developed by Fowler we may write (Fowler, Eq. (438))

$$\ln p = -\frac{\lambda_0}{RT} + \frac{(C_p)_0}{R} \ln T + \ln \frac{(2\pi m)^{3/2} k^{5/2}}{h^3} + \ln R(T) V(T) - \ln K(T) + \ln R(0) V(0) - \ln K(0), \quad (3)$$

[2] R. H. Fowler, Statistical Mechanics, Cambridge University Press, Cambridge, 1929.

where $R(T)$ = rotational vapor partition function at temperature T, $V(T)$ = vibrational partition function at temperature T, $K(T)$ = crystal partition function at temperature T, $R(0)$ = rotational vapor partition function at temperature 0°K, $V(0)$ = vibrational partition function at temperature 0°K, $K(0)$ = crystal partition function at temperature 0°K. The value of the partition function at $T=0$°K must remain in our equation because by definition the partition functions have been constructed to start out with a constant term.

We may now apply this equation to the case of crystalline benzene in the temperature range of 100°–298°K. Under these special conditions we may make the following changes in Eq. (3):

(1) In the case of a polyatomic molecule like benzene with moments of inertia as large as 10^{-38}, the rotational degrees of freedom are fully excited at temperatures above 10°K. Then $(C_p)_0=4R$ and the rotational partition function is then identical with the classical value:

$$R(T)=8\pi^2(8\pi^3ABC)^{1/2}(kT)^{3/2}/h^3.$$

(2) Vibration is contributing to the heat capacity but has not attained the classical value and must be calculated from

$$V(T)=\sum_1^f \frac{1}{1-\exp(-h\nu_f/kT)}$$

where the summation is over the f modes of vibration having $(3n-6)$ degrees of freedom.

(3) The crystal partition function, $K(T)$ is to be discussed from thermodynamic relationships. It has been shown by Fowler (page 128) that any crystal containing the average number $\bar{P}$ molecules with a partition function $K(\theta)$ and average energy $\bar{E}$, contributes to the entropy of the crystal by the following amount:

$$S_{(s)}=k[\bar{P}\ln K(\theta)-\bar{E}_{(s)}\ln\theta].$$

We may change the independent variable θ to T (the absolute temperature) by the known relationship between the two, $\theta=e^{-1/kT}$. Then for a mole of the crystal:

$$S_{(s)}=R[\ln K(T)+\bar{E}_{(s)}/T]$$

or

$$\ln K(T)=S_{(s)}/R-\bar{E}_{(s)}/RT.$$

By definition

$$\bar{E}_{(s)}-\bar{E}_s{}^0=\int_0^T C_{v(s)}dT$$

$$\frac{\bar{E}_{(s)}}{RT}=\frac{1}{RT}\int_0^T C_{v(s)}dT+\frac{E_{(s)}{}^0}{RT}.$$

But $E_{(s)}{}^0/RT$ is the first term in the crystal partition function and therefore equal to $\ln K(0)$. Hence

$$\ln K(T)=-\frac{1}{RT}\int_0^T C_{v(s)}dT+\frac{S_{(s)}}{R}-\ln K(0).$$

(4) Fowler has shown that if we ignore electronic structure and treat the atoms as structureless mass points, then: $K(0)=V(0)=1$.

(5) $R(0)=\tilde{\omega}_0\delta/\sigma$.

It is assumed that the energy in the lowest rotational state is equal to zero so that both $\tilde{\omega}_0$ and δ will have the value of unity.

With these expressions for the partition functions we obtain:

$$\ln p=-\frac{\lambda_0}{RT}+\frac{4R}{R}\ln T+\ln\frac{(2\pi m)^{3/2}k^{5/2}}{h^3}+\ln\left[\sum_1^f\frac{1}{1-\exp(-h\nu_f/kT)}\right]+\ln\frac{8\pi^2(8\pi^3ABC)^{1/2}(kT)^{3/2}}{h^3}+\frac{1}{RT}\int_0^T C_{v(s)}dT-\frac{S_{(s)}}{R}+\ln\frac{\tilde{\omega}_0\delta}{\sigma}. \quad (4)$$

Our problem, then, is to substitute in this equation the experimentally determined values of the vapor pressure and other physical constants and to solve for the values of the symmetry number contained in the last term.

We may take as the first step the calculation of the vibrational contribution of the specific heat. It is necessary to know this, first, in order to extrapolate the specific heat curve of the solid to 0°K, and second, in order to calculate the specific heat of the vapor, for which experimental measurements are not available.

The best source of data for this calculation lies in the frequencies observed in the Raman spectra. With the help of the mechanical models of molecules developed by Kettering, Shutts and An-

TABLE II.

Benzene		Cyclohexene			
Ring vibration	Degrees of freedom	Ring vibration	Degrees of freedom		Degrees of freedom
400 cm^{-1}	2	171 cm^{-1}	1	1263	1
605	1	282	1	1426	5
849	2	390	1	1443	5
991	6	445	1	1650	5
1178	1	487	1	C-H	
C-H		635	1	stretching	
bending		656	1	2635	1
1584	6	821	1	2660	1
1605	6	873	1	2833	2
C-H		904	1	2856	1
stretching		963	1	2873	1
2947	1	1034	1	2908	1
3047	2	C-H		2934	1
3060	2	bending		2986	1
3185	1	1062	1	3020	1
	—	1134	1		—
	30	1218	1		42
		1238	1		

drews[3] it is possible to assign values for the number of degrees of freedom associated with each Raman frequency. Table II gives the values so assigned, the frequencies being those observed by Wood and Collins.[4] The specific heat term associated with each frequency at various temperatures can be calculated with the help of the Einstein specific heat function. When multiplied by the appropriate factors to take into account the number of degrees of freedom associated with each frequency, the sum of these results gives the total contribution of vibration to the heat capacity of the molecule. These assignments of degrees of freedom are not exact but it is believed that they give the correct order of distribution of frequencies with an accuracy sufficient for this calculation.

In extrapolating the heat capacity curve of the solid to 0°K it is also necessary that one know the characteristic temperature, θ_m, for the molecules vibrating as units in the crystal lattice, i.e., excluding internal molecular vibration. This frequency when substituted in the modified Debye equation for the heat capacity of a solid yields the so-called Debye contribution to the heat capacity. This frequency may be calculated most conveniently by the Lindemann melting point formula. The modifications necessary to apply this treatment to a molecular crystal lattice have been discussed by Andrews.[5] From the Lindemann formula it is found that for benzene, $\theta = 159$, and for cyclohexane, $\theta = 133$. With these values, C_p has been calculated for the lattice vibrations in the temperature range below available experimental values.

The difference of $C_p - C_v$ for the solid was calculated according to Andrews' modifications of Nernst's formula:

$$C_p - C_v = (C_v)^2 (T/T_m)(0.0214)$$

where (C_v) is the specific heat at constant volume arising from the Debye terms mentioned above,

[3] C. F. Kettering, L. W. Shutts and D. H. Andrews, Phys. Rev. [2], **36**, 531 (1930).

[4] Wood and Collins, Phys. Rev. [2], **42**, 386 (1932).

[5] D. H. Andrews, Chem. Reviews **5**, 533 (1928).

TABLE III. *Benzene.*

	Einstein (Solid and vapor)		Debye		— — — — — Condensed Phase — — — — —			
		C_p	(Solid)	Expansion	Calc.	Experimental		
T	C_v	(Vapor)	C_v	(Solid)	C_v	C_p	S	H
10	0	8.0	0.24	0	0.24	0.3	0.01	0.8
20	0	8.0	1.67	0	1.7	1.7	0.57	9.9
30	0	8.0	4.00	0.05	4.1	4.5	1.68	40.0
40	0	8.0	6.06	0.11	6.2	6.6	3.27	95.0
50	0.02	8.02	7.54	0.22	7.8	8.0	4.92	169.0
60	0.06	8.06	8.56	0.34	9.0	9.4	6.51	257
80	0.26	8.26	9.86	0.6	10.8	11.1	9.41	465
100	0.64	8.64	10.54	0.85	12.0	12.0	11.95	695
120	1.1	9.1				13.30	14.25	947
140	1.70	9.7				14.80	16.42	1227
160	2.4	10.4				16.33	18.52	1538
180	3.0	11.0				18.04	20.54	1881
200	4.0	12.0				20.10	22.50	2556
220	4.6	12.6				22.34	24.48	2680
250	6.1	14.1				26.15	27.59	3402
280	7.6	15.6				31.44	39.39	6652
300	8.7	16.7				32.33	41.59	7290
350	11.6	19.6				35.9	46.84	8993

TABLE IV. *Cyclohexene.*

T	Einstein (Solid and vapor) C_v	C_p (Vapor)	Debye (Solid) C_v	Expansion (Solid)	Condensed Phase — Calc. C_v	Condensed Phase — Experimental C_p	S	H
10	0	8.0	0.4	0	0.4		0.05	1.0
20	0	8.0	2.6	0	2.6		0.79	13.0
30	0	8.0	5.3	0.08	5.4		2.18	52.0
40	0.2	8.2	7.3	0.2	7.9		3.90	119
50	0.4	8.4	8.6	0.4	9.4		6.58	205
60	0.7	8.7	9.4	0.6	10.7		7.42	306
80	1.4	9.4	10.4	1.0	12.9		10.61	535
100	2.30	10.3	10.9	1.2	14.2	13.2	13.5	787
120	3.29	11.3				14.85	16.06	1067
140	4.28	12.3				21.4	25.50	2360
160	5.35	13.35				24.3	28.7	2815
200	7.67	15.7				28.0	39.3	4674
250	10.87	18.9				30.8	45.9	6141
300	14.35	22.35				34.3	51.7	7763
350	18.51	26.7				37.7	57.15	9560

T is the temperature at which computations are being made, and T_m is the melting point of the crystal.

Tables III and IV give the heat capacity, entropy and relative heat content values which are based on the recent work of Parks and Huffman,[6] and the extrapolated values calculated in the manner described above. It may be seen that the calculated values of the heat capacity of the solid check the experimental values fairly well at the temperatures below which it is necessary to use calculated values for extrapolation.

In regard to the moments of inertia of the two substances under consideration, it seems best to use calculated values, as the values that might be obtained from a study of band spectra are very uncertain. For benzene the plane hexagonal model is assumed with the distance between the carbon atoms equal to 1.42A. This is done in view of the fact that for graphite the C–C distance is 1.44A, and for hexa-methyl benzene 1.42A. The hydrogens are considered to be on the extension of the diagonal line, 1.2A away from the carbon atoms. There is no existing x-ray data as to these dimensions determined directly from benzene itself. The calculated results are given in Table V.

For cyclohexene a plane hexagon is also taken as the basis of calculation, five sides being 1.54A long and the sixth side 1.35A, the latter being the carbon-carbon separation in double bonds. The hydrogens are assumed to be 1.2A from the carbons. While it is probable that benzene and cyclohexene are not representable by a plane model a calculation on this assumption is not too far from the actual state of affairs and the difference in the numerical values obtained in either case is small.

TABLE V. *Moments of inertia.*

	Benzene	Cyclohexene
A	154×10^{-40}	197×10^{-40}
B	154×10^{-40}	213×10^{-40}
C	308×10^{-40}	395×10^{-40}
(ABC)	7.42×10^{-114}	16.59×10^{-114}

The values of the vapor pressure are taken from the work of Deitz[7] which was carried out in order to make these calculations possible.

The only other values necessary to complete the calculation are those of $V(T)$. These values as calculated from $V(T)=[1-\exp\ (-h\nu/kT)]^{-1}$ are given in Table VI.

With the aid of the above data calculations for the value of the symmetry number have been made from Eq. (4), and are given in Table VI.

In examining the results of these calculations we may note in the first place that the symmetry number stays reasonably constant over a wide range of temperature. This is a test of the accu-

[6] G. S. Parks and H. M. Huffman, J. Am. Chem. Soc. **52**, 1032 (1930).

[7] V. Deitz, J. Am. Chem. Soc. (1933). Shortly to be published. The values of the heat of sublimation (λ_0) at 0°K were calculated as 12,302 cal for benzene; 11,333 cal for cyclohexene. These values are based on the heats of vaporization reported by Mathews, J. Am. Chem. Soc. **48**, 562 (1926), the heats of fusion reported by Parks (reference 6), and the heat capacities in the above table.

TABLE VI.

Substance	Temp.	ln $V(T)$	Sym. number
Benzene (s)	100°K	0.0000	5.4
" (s)	200°	0.0901	6.0
" (s)	250°	0.1503	6.3
" (s)	278.5	0.1972	6.9
" (l)	278.5	0.1972	6.5
" (l)	298	0.2466	5.5
Cyclohexene (s)	100°	0.0493	1.8
" (l)	298°	0.6316	2.2

racy of the estimates of the heat capacities, and indicates that these values are satisfactory for the present purpose.

In order to extend the temperature range as far as possible, two calculations for liquid benzene and one for liquid cyclohexene have been included. Over this large temperature range one might expect considerable change in the conditions which affect the validity of the various assumptions upon which Eq. (4) is based. The fact that the symmetry numbers remain so constant is an indication that these assumptions are justified to a considerable extent, and that the results secured are not fortuitous.

In order to illustrate the sensitivity of the value of symmetry number to changes in the experimental data, the following calculation was made with the data at 200°K. If the value of ABC, the product of the three moments of inertia, is in error by 10 percent, the error in the symmetry number, $\Delta\sigma$, is 0.2. If the entropy of the solid is in error by 2 percent, $\Delta\sigma$ is 1.2. If the temperature is in error by 2°, $\Delta\sigma$ is 1.0. If λ_0 is in error by 2 percent, $\Delta\sigma$ is 1.0. Again if $V(T)$ is in error by 10 percent, $\Delta\sigma$ is 0.2. Finally if the vapor pressure data are off by 10 percent, $\Delta\sigma$ is 0.3.

The absolute value of the symmetry numbers suggests immediately that we are dealing not with a plane hexagon but with a puckered ring. It is true that the majority of the evidence from dipole measurements and x-rays has been in favor of a flat benzene ring. We are dealing here, however, with a property that may well be much more sensitive than either of the above in detecting lack of symmetry of the ring. The value six seems to show that there are but three rather than six equivalent positions on one side of the ring. It is impossible to say whether this is due to a staggering of the hydrogens or to a puckering of the ring. It seems significant however, that the number six should be indicated so definitely. The result of a symmetry number of two for cyclohexene tends to confirm the validity of the conclusion.

In conclusion it may be pointed out that this provides a method for calculating the absolute vapor pressure from the thermal and statistical properties of the molecule. It appears that symmetry may play an important part in determining the physical properties of a molecule and perhaps the chemical behavior as well.

Binding Energies in the Growth of Crystal Nuclei from Metallic Atoms

HUGH S. TAYLOR, HENRY EYRING AND ALBERT SHERMAN, *Frick Chemical Laboratory, Princeton University*

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First order perturbation theory has been employed to compute the binding energies of various geometrical configurations of three to eight atoms of sodium. It has been assumed that in the metal lattice the binding is essentially homopolar. It has been shown that the growth of a unit cell probably proceeds via the diatomic molecule to a square, a fifth atom adding along a cube edge, a sixth at the body center and the cell completed by location of atoms at the remaining cube corners. The unit cell is still a very unstable unit, a result in agreement with high vapor pressures and solubility of finely divided particles, and with the concept of active centers on reaction surfaces. The fifth order secular equation employed to determine the energies of configurations of five and six atoms has been made more amenable to use in calculations. A fourteenth order secular equation, with similar characteristics, has been employed for the cases of seven and eight atoms. Approximate calculations with copper atoms instead of sodium give similar results but indicate that higher activation energies of nuclei formation may obtain in this case. The percentage of the total binding assigned to interchange is shown to be an important factor. The calculations indicate that the net effect of interchange forces in homopolar crystals is to increase the potential energy. The crystal structure is stable only because of the coulombic and van der Waals' forces. When applied to hydrogen (90 percent interchange) it is shown that a metallic lattice is utterly unstable.

THE recent development in the application of quantum mechanics to problems of chemical reaction, with the exhibition in terms of modern theory of the well-known chemical concept of activation energy has prompted the present inquiry into the problem of the association of metallic atoms to form a lattice structure. Numerous data drawn from the fields of electrode phenomena and surface reactions indicate that many of the properties of metallic surfaces are a function of the position of the atoms in the surface layer. It is also known that the surface structure is sensitive to the influence of temperature, that, therefore, the concept of activation energy is applicable to processes operative during changes of surface structure. The sintering of catalysts is one piece of experimental evidence. The concept of centers of abnormal activity on such surfaces is also indicative of positions in the surface of high potential energy. The type of adsorption, whether van der Waals' or activated adsorption, which occurs on these surfaces is governed in part by the arrangement of atoms in the surface layers as is evident from recent quantum mechanical examination of this phenomenon.[1] It was, therefore, of interest to examine how far the application of first order perturbation theory could be utilized to exhibit such characteristics of a metallic surface.

In addition, also, to the subjects already mentioned the properties of small particles have a quite general physico-chemical interest. We need only recall, for example, in this connection, the extensive work on the increased solubility of fine particles, first emphasized by the researches of Hulett[2] on the solubility of barium sulphate. Such increased solubility is paralleled by the high values found for the vapor pressures of condensed films of metals on surfaces such as glass, with correspondingly small heats of vaporization of such films. These latter data are more pertinent to the problem which we have had under consideration. As was shown by Estermann[3] the condensation of cadmium vapor on glass, copper and silver gave films whose heats of vaporization (3000–5000 calories) represent only 1/5 to 1/7 that of bulk crystalline cadmium. Frenkel[4] has pointed out that such films are to be regarded as composed of "twins" and that the first nuclei of such film growth are diatomic aggregates. Our calculations should serve to show something of the transition states from such twins to the macroscopic crystals.

[1] (a) M. Polanyi, Zeits. f. Elektrochemie **35**, 561 (1929). (b) J. E. Lennard-Jones, Trans. Faraday Soc. **28**, 333 (1932). (c) A. Sherman and H. Eyring, J. Am. Chem. Soc. **54**, 2661 (1932).

[2] G. A. Hulett, Zeits. f. physik. Chemie **37**, 385 (1901); **47**, 357 (1904).

[3] I. Estermann, Zeits. f. Elektrochemie **31**, 441 (1925).

[4] J. Frenkel, Zeits. f. Physik **26**, 117 (1924).

Slater[5] has already discussed the problem of the properties of the metallic lattice of sodium. He has thus shown that the perturbation method is capable of yielding an approximation to actual observed properties, so that the method of treatment inspires some confidence that a more detailed examination from a somewhat different standpoint might produce other fruitful results. Slater treated in particular detail the problem of many atoms in a linear assembly or filament. To do this it was necessary to neglect terms which arise from atoms more distant than neighbors. By restricting attention to fewer atoms it is possible to consider all interactions and to treat in the same detail configurations other than filaments. The method used is that employed by Slater[6] for three and four atoms and since extended[7] to as many as eight atoms, which represents the maximum number here considered. Our study differs from recent investigations of Kossel[8] and Stranski[9] on crystal growth in that their work deals principally with ionic lattices and actual crystals. We have confined our attention to metal atoms and the initial stages of formation of a crystal unit. Our limitation of the problem to that of a few atoms is dictated mainly by the inherent difficulty of the many-atom problem, but also because, with more atoms, terms other than the coulombic and interchange become increasingly important. Such terms may be thought of as involving the simultaneous interchange of more than two electrons.

It was not expected that such calculations would yield information concerning crystallization of metals in bulk at high temperatures. Rather we have sought to examine theoretically the phenomena occurring with films of metallic atoms laid down at low temperatures and which show processes of incipient crystallization on raising to moderate temperatures; for example, phenomena such as those of Estermann already mentioned and those studied by Langmuir in the change of properties of molybdenum films deposited on glass at liquid air temperatures, the characteristics of which are in part destroyed by raising the film to room temperature.[10] Films of iron behave similarly.[11] The processes known as "sintering" in the study of catalysts have certain analogies to such changes in films. In each case the experimental evidence points to the existence of definite, if small, activation energies.

Procedure

At the outset we shall present the procedure which we have followed with reference to the element sodium. We shall do so because it is a case already considered by Slater for material in bulk. Also, for this element, the data for the binding energies of the sodium molecule and the ratio of interchange to coulombic binding as deduced by Rosen[12] represent, at the present time, the most trustworthy data for any metallic vapor with the possible exception of lithium. We have calculated the total binding energy of systems composed in the main of 3, 4, 5 and 6 metal atoms and have explored the additional possibilities obtaining with 8 atoms. We have examined the binding energies of these systems for a variety of geometric configurations chosen to exhibit the stages in which the formation of a metallic lattice might be achieved.

For the simpler systems we have made use of the roots of the secular equations for three atoms, E_3, and four atoms, E_4,

$$E_3=A+B+C+[\tfrac{1}{2}((\alpha-\beta)^2+(\alpha-\gamma)^2+(\beta-\gamma)^2)]^{1/2}, \quad (1)$$

$$E_4=A_1+A_2+B_1+B_2+C_1+C_2+[\tfrac{1}{2}((\alpha_1+\alpha_2-\beta_1-\beta_2)^2+(\alpha_1+\alpha_2-\gamma_1-\gamma_2)^2+(\beta_1+\beta_2-\gamma_1-\gamma_2)^2)]^{1/2}, \quad (2)$$

which have already been employed by one of us[13] in the computation of activation energies of reaction between atoms and molecules as well as between two diatomic molecules. Additional evi-

[5] J. C. Slater, Phys. Rev. [2], **35**, 509 (1930).
[6] J. C. Slater, Phys. Rev. [2], **38**, 1109 (1931).
[7] Reference 1(c) and forthcoming publications.
[8] W. Kossel, Machr. Ges. Wiss. Gottingen, 1927, p. 135; Leipziger Vortrage, 1928, p. 1.
[9] I. N. Stranski, Zeits. f. physik. Chemie **136**, 259 (1928); **17B**, 127 (1932).
[10] I. Langmuir, J. Am. Chem. Soc. **41**, 167 (1919).
[11] W. Frankenburger and K. Mayrhofer, Zeits. f. Elektrochemie **35**, 590 (1929); **37**, 473 (1931).
[12] N. Rosen, Phys. Rev. [2], **38**, 255 (1931).
[13] H. Eyring and M. Polanyi, Zeits. f. physik. Chemie **12B**, 279 (1931). H. Eyring, J. Am. Chem. Soc. **53**, 2537 (1931).

dence of the applicability of such formulae is furnished by the recent calculations of Pelzer and Wigner[14] concerning the ortho-para hydrogen conversion, from which not only the activation energy but also the actual rate of reaction has been successfully derived.

For five and six atoms the more complex fifth order secular equation recently published[15] has been rendered more amenable to calculation by employing eigenfunctions which are orthogonal to the degree of approximation used in the 3–4 atom calculations. The first eigenfunction of the earlier work was retained here and the subsequent functions were each in turn made orthogonal to those which preceded it, according to the well-known method of Schmidt.[16] This yielded a fifth order determinant, $|H_{ij}-d_{ij}E|=0$, with the elements given in Table I.

The use of Table I is at once apparent from the following single example: $H_{11}=4C+4ab-2ac-2ad-2ae-2bc-2bd-2be+4cd-2ce-2de-2af-2bf-2cf-2df+4ef$. Here, C is the total coulombic binding of six atoms situated in any configuration *abcdef* under study; *ab*, *ac*, *ad*, etc., represent the interchange integrals between the two atoms so designated, and determined by the energy of binding of the two atoms at the given distance as derived from a Morse potential energy curve for a diatomic molecule. This table determines all the elements when it is remembered that $H_{ji}=H_{ij}$. The values of d_{ij} in the determinant have the same values as the coefficients of C in the corresponding H_{ij}; thus, $d_{11}=4$, $d_{22}=3$ and so on. It will be noted that $d_{ij}=0$ (for $i\neq j$) because of the orthogonality of our eigenfunctions. Inspection of Table I will further reveal that with systems possessing a reasonable degree of symmetry, by suitable assignment of letters to particular positions in the configuration, many of the non-diagonal elements may become zero. Thus, for example, in a configuration composed of four atoms *abcd* forming a square with a fifth atom, *e*, at the face center and the sixth atom, *f*, at infinity, thus reducing it essentially to a five atom problem, the symmetry is such that the fifth order determinant reduces at once to a quadratic expression, the roots of which are $C-2ac$ and $C-2ab$, the other three roots of the quintic being $\frac{1}{4}H_{11}$, $\frac{1}{3}H_{22}$, and $\frac{1}{3}H_{33}$. Since the coulombic and interchange integrals are negative the lowest root is obviously $C-2ab$ if *ab* is a diagonal of the square configuration, *ac* a side of the same. Additional examples of such simplification will be noted in the presentation of results.

TABLE I.

	H_{11}	H_{22}	H_{33}	H_{44}	H_{55}	H_{12}	H_{13}	H_{14}	H_{15}	H_{23}	H_{24}	H_{25}	H_{34}	H_{35}	H_{45}
C	+4	+3	+3	+2.25	+2	0	0	0	0	0	0	0	0	0	0
ab	+4	+3	−3	−2.25	−2	0	0	0	0	0	0	0	0	0	0
ac	−2	−1.5	+1.5	+1⅛	−2	0	−3	0	0	0	−2¼	0	0	0	0
ad	−2	−1.5	+1.5	−1⅞	+⅔	0	+3	0	0	0	−¾	+2	0	0	−1
ae	−2	−1.5	−1.5	+⅜	+⅔	0	0	−½	−2	−½	+½	−1	−½	+1	+½
bc	−2	−1.5	+1.5	+1⅛	−2	0	+3	0	0	0	+2¼	0	0	0	0
bd	−2	−1.5	+1.5	−1⅞	+⅔	0	−3	0	0	0	+¾	−2	0	0	−1
be	−2	−1.5	−1.5	+⅜	+⅔	0	0	+½	+2	+½	−½	+1	−½	+1	+½
cd	+4	−3	−3	−¾	+⅔	0	0	0	0	0	0	0	0	0	+2
ce	−2	+1.5	−1.5	−1⅞	+⅔	−3	0	0	0	0	0	0	+¾	−2	−1
de	−2	+1.5	−1.5	+1⅛	−2	+3	0	0	0	0	0	0	+2¼	0	0
af	−2	−1.5	−1.5	+⅜	+⅔	0	0	+½	+2	+½	+½	−1	+½	−1	+½
bf	−2	−1.5	−1.5	+⅜	+⅔	0	0	−½	−2	−½	−½	+1	+½	−1	+½
cf	−2	+1.5	−1.5	−1⅞	+⅔	+3	0	0	0	0	0	0	−¾	+2	−1
df	−2	+1.5	−1.5	+1⅛	−2	−3	0	0	0	0	0	0	−2¼	0	0
ef	+4	−3	+3	−2¼	−2	0	0	0	0	0	0	0	0	0	0

For seven and eight atoms the procedure is to be detailed elsewhere. It is essentially similar to the cases already discussed, but, even with the simplifications noted, the determinant received is of the fourteenth order, the roots of which are the energies of the fourteen singlet states of the seven or eight atoms in the given configuration. It is obvious that the computations involved severely restrict the number of such examples

[14] H. Pelzer and E. Wigner, Zeits. f. physik. Chemie **15B**, 445 (1932).

[15] Reference 1(c).

[16] Courant-Hilbert, *Methoden der Mathematischen Physik*, 2d edition, p. 41, Springer.

studied. In all cases, the lowest root, algebraically, corresponds to the lowest energy of such a configuration and, therefore, the most favored energy level of the system. Where necessary, graphical representation of the value of the determinant with arbitrarily assigned values for the energy permits the finding of the lowest energy value at which the determinant becomes zero.

In addition to sodium, we have attempted also to apply the procedure to copper. We are aware of the arbitrary nature of some of our assumptions in this case, but wished to explore a metal, possessing different lattice features (face centered cubic) from those of sodium, and of which, from the data of surface catalysis, we know something concerning surface changes on sintering. We have also examined the case of hydrogen in a similar manner for the purpose of exhibiting the properties of a substance which definitely forms molecular rather than atomic lattice structure.

We have neglected the influence of van der Waals' forces, in the calculations up to eight atoms. The additive nature of both the van der Waals' and the coulombic forces implies that both are in principle involved in that portion, C, of our total energies normally assigned to coulombic forces. In the case of copper it was necessary, in the absence of definite data, to assign an arbitrary fraction of the total to the coulombic portion. We have, however, in this case, traced the influence of changes in this fraction on the values of energies obtained for various configurations. These will be presented in the subsequent sections.

Results

I. Sodium

The binding energies of two atoms at any distance have been derived from a Morse curve set up from the following data, $D_{Na_2}=17.5$ k.cals., $\omega_0=159$ cm^{-1} and $r_0=3.15$A. For the coulombic binding C we have used Rosen's value[12] of 28.3 percent of the total binding and have indicated it by a subscript, $C_{28.3}$. The interchange factor is then 0.717 giving the interchange energy, $I_{71.7}$. With this material the following results were obtained for various possible configurations.

1. Three atoms. (*a*) *Linear configuration:* With the aid of Eq. (1) which reduces to $E_a=2A+B+\alpha-\beta$, the following data were obtained:

r	2.6	3.15	3.25	3.43	3.7	4.25	4.8
$C_{28.3}$	−8.2	−10.7	—	−10.1	−8.9	−6.5	−4.4
$I_{71.7}$	−4.2	−10.9	—	−11.0	−10.2	−7.8	−5.5
E	−12.4	−21.6	−21.8	−21.1	−19.1	−14.3	−9.9

2. Four atoms. (*a*) *Linear configuration:* The energy of a system of four atoms in a line, equally spaced, was determined, by means of Eq. (2), which reduces to

$$E_a=3A+2B+C+[\tfrac{1}{2}((\alpha-\gamma)^2+(\alpha-\beta)^2+(\alpha+\gamma-2\beta)^2)]^{1/2}$$

as a function of increasing interatomic distance, r. The data so obtained were:

r	2.6	3.15	3.25	3.43	3.70	4.25	4.80
$C_{28.3}$	−13.4	−16.45	—	−15.3	−13.6	−9.85	−6.7
$I_{71.7}$	−8.1	−18.9	—	−19.2	−17.7	−13.5	−9.5
E	−21.5	−35.4	−35.7	−34.5	−31.3	−23.4	−16.2

The lowest figure in the preceding data for E and in all subsequent tabulations represents the value obtained by interpolation from a graph of the other calculated data.

(*b*) *Square configuration:* The equation in this case simplifies to:

$$E_b=2[2A+C+0.717(A+\alpha-(C+\gamma))],$$

from which the following data are derived:

r	2.6	3.15	3.3	3.43	3.7	4.25	4.8
$C_{28.3}$	−22.0	−25.6	—	−23.4	−20.5	−14.6	−9.7
$I_{71.7}$	+5.5	−11.2	—	−13.6	−13.7	−11.7	−8.8
E	−16.5	−36.8	−37.7	−37.0	−34.2	−26.3	−18.5

(*c*) *Cubic arrangement:* The atoms occupy four adjacent corners of a cube of side r. The equation simplifies so far that all interchange energy is absent. $E_c=3(A+B)$, and yields the values:

r	2.6	2.9	3.15	3.43	3.7	4.25	4.8
$E=C_{28.3}$	−23.0	−24.9	−23.5	−20.8	−17.8	−12.3	−8.0

(*d*) *Regular tetrahedral configuration:* The tetrahedron of side r also gives an equation from which the interchange energy is absent, $E_d=6A$. The values can obviously be derived immediately from a Morse curve by multiplication with the factor 1.7 ($=6\times0.283$).

r	2.6	3.15	3.43	3.7	4.25	4.8
$E=C_{28.3}$	−19.8	−30.1	−28.8	−26.0	−19.2	−13.2

(*e*) *Linear configuration, abc, with d at right angles to abc at a:* This configuration calculated by means of Eq. (2) gives:

r	2.6	3.15	3.43	3.7	4.25	4.8
$C_{28.3}$	−16.9	−18.9	−17.2	−15.0	−10.6	−7.1
$I_{71.7}$	−5.2	−14.7	−15.7	−15.0	−11.9	−8.55
E	−22.1	−33.6	−32.9	−30.0	−22.5	−15.7

(*f*) *Linear configuration, abc, with d at right angles to abc at b:* This configuration gives similarly: $E_f = 3A + 2B + C + \alpha - \gamma$.

r	2.6	3.15	3.43	3.7	4.25	4.8
$C_{28.3}$	−20.3	−21.3	−19.1	−15.5	−11.5	−6.1
$I_{71.7}$	−4.2	−10.9	−11.1	−10.2	−7.8	−4.5
E	−24.5	−32.2	−30.2	−25.7	−19.3	−10.6

3. Five atoms. (*a*) *Face centered square:* The fifth atom *e* is at the center of a square *abcd*. The symmetry of this configuration is such that $I_{71.7} = -0.717$ (2*ab*). In this and succeeding tables r refers to the length of side of the square in angstroms.

r	3.68	3.8	4.0	4.2	4.4	4.95
$C_{28.3}$	−33.9	−36.0	—	−34.5	−33.1	−27.4
$I_{71.7}$	+8.3	+7.3	—	+4.7	+3.8	+2.0
E	−25.6	−28.7	−30.6	−29.8	−29.3	−25.4

(*b*) *Five atoms at face and center of body centered cube:* The equation is identical with that of the preceding example. The dimensions, however, at the minimum may be especially noticed.

r	3.3	3.60	3.68	4.0	4.53	4.95
$C_{28.3}$	−43.3	—	−40.8	−36.8	−27.5	−21.5
$I_{71.7}$	+12.3	—	+8.3	+5.8	+3.2	+2.0
E	−31.1	−32.6	−32.5	−31.0	−24.3	−19.5

(*c*) *Five atoms at cube corners, with four on one face:* The best arrangement of letters for the solution of the determinant calls for *acbd* as the face, with *a* diagonal to *b*, and *e* symmetrical to *a* and *b*. This symmetry yields a fifth order determinant which factors into a quadratic and a cubic equation of which the lowest root is found in the cubic.

r	2.8	3.0	3.2	3.4	3.7	4.0
$C_{28.3}$	−40.3	−39.0	−36.9	−33.8	−29.1	−24.4
$I_{71.7}$	+13.4	+6.5	+1.2	−2.7	−5.5	−7.7
E	−26.9	−32.5	−35.5	−36.5	−34.6	−32.1

(*d*) *Four atoms, on square, fifth on diagonal extension at distance 0.707r:* The best arrangement of letters calls for *acbe* as the face, *a* diagonal to *b*, *d* on the extension of *ce*. This also yields a determinant which factors into a quadratic and a cubic equation.

r	3.43	4.0	4.25	4.53	4.80
$C_{28.3}$	−27.1	−23.6	−20.6	−17.7	−15.1
$I_{71.7}$	+6.3	−10.1	−11.0	−11.9	−11.6
E	−20.8	−33.7	−31.6	−29.6	−26.7

4. Six atoms. (*a*) *Five atoms at cube corners, sixth at body center:* The configuration employed showed *afbd* as the atoms on the cube face, atom *e* was at the fifth cube corner and adjacent to *d*; the body centered atom was *c*.

r	3.0	3.2	3.4	3.7	4.95
$C_{28.3}$	−55.2	−59.4	−58.0	−54.0	−27.1
$I_{71.7}$	+14.8	+12.5	+9.5	+7.2	+2.0
E	−40.4	−46.9	−48.5	−46.8	−25.1

(*b*) *Six atoms at cube corners forming two faces:* The two cube faces were labeled *afbe* and *fbcd*. In this way maximum simplification was obtained but the resultant determinant was still fifth order.

r	2.5	2.8	3.0	3.2	3.7	4.0
$C_{28.3}$	−46.6	−59.2	−56.8	−53.6	−41.8	−34.9
$I_{71.7}$	+10.3	+22.0	+20.8	+19.1	+14.4	+12.0
E	−36.3	−37.2	−36.0	−34.5	−27.4	−22.9

5. Eight atoms. (*a*) *Seven atoms at cube corners, eighth at the body center:* For this configuration four solutions were obtained each involving a 14th order determinant. The data gave a minimum at 3.4A.

r	3.15	3.4	3.7	4.3
$C_{28.3}$	−104.9	−99.7	−90.1	−65.8
$I_{71.7}$	+38.9	+31.5	+24.7	+16.8
E	−66.0	−68.2	−65.4	−49.0

(*b*) *Eight atoms at cube corners:* Four solutions of this configuration were obtained. It is evident that the increased symmetry of the complete cube gives the configuration a greater stability than that possessed by system 4*b* of six atoms at cube corners.

r	2.9	3.0	3.15	3.25
$C_{28.3}$	−106.9	−104.0	−99.3	−94.4
$I_{71.7}$	+53.8	+42.5	+31.2	+27.4
E	−53.1	−61.5	−68.1	−66.9

We present a graphical summary of some of these calculations in Figs. 1, 2, 3 and 4.

II. Copper

For this element we have constructed a Morse curve using the following estimated data $D_{Cu_2} = 56$ k.cals., $\omega_0 = 248$ cm^{-1} and $r_0 = 2.18$A. The heat of dissociation of the molecule was assumed to be the same fraction of the heat of sublimation ($\lambda = 82.06$ k.cals.)[17] that the dissociation energy of the sodium molecule is of the heat of sublimation of sodium. The equilibrium distance, r_0, was deduced from those of copper

[17] H. A. Jones, I. Langmuir and G. M. J. Mackay, Phys. Rev. [2], **30**, 201 (1927).

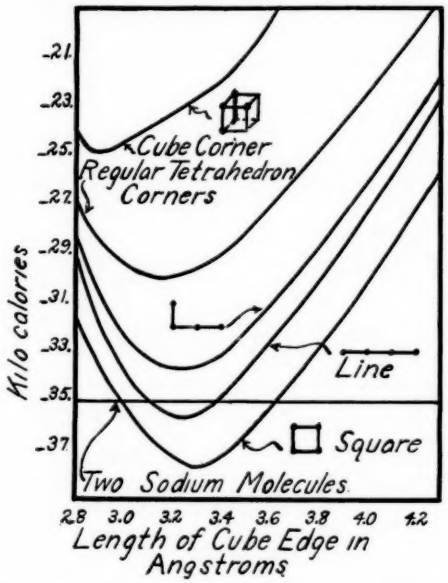


FIG. 1. Binding energies of four atom configurations.

hydride and hydrogen ($2r_{0CuH} - r_{0H_2}$). For the value of ω for copper, it was assumed that it bore the same ratio to that of sodium that the characteristic temperatures of the two elements possess in the evaluation of the specific heat data.

We present graphically in Figs. 5a and 5b the data for a 4 atom linear configuration, a square and a 5 atom face centered square with two assumptions as to the fraction of coulombic binding. In Fig. 5a this is assumed to be 20 percent; in Fig. 5b the fraction is 30 percent. It will readily be seen that the general nature of the results is the same as in the case of sodium. The actual magnitudes of the energy differences at the minima are in each case much greater than with sodium and are very much larger with the assumption of 20 percent coulombic binding.

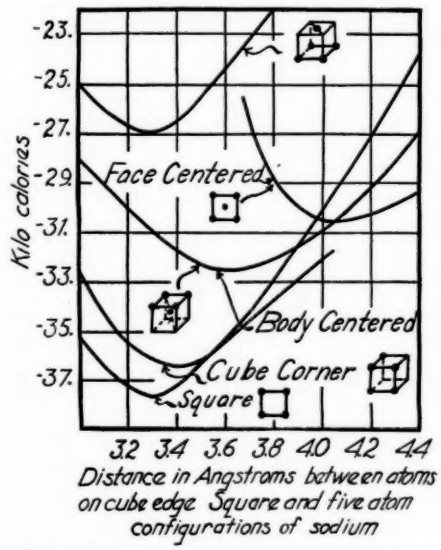


FIG. 2. Binding energies of five atom configurations.

III. Hydrogen

To illustrate the fundamental importance of the coulombic : interchange ratio thus evident we have made calculations of the binding energies of various configurations of 4 and 6 atoms of hydrogen, using the 10 : 90 ratio that has been assumed in earlier work on the homogeneous reactions involving hydrogen.[13] The Morse curve data in this case were $D_{H_2} = 101.5$ k.cals., $\omega_0 = 4262$ cm^{-1}; $r_0 = 0.76$A.[13] Table II summarizes the data.

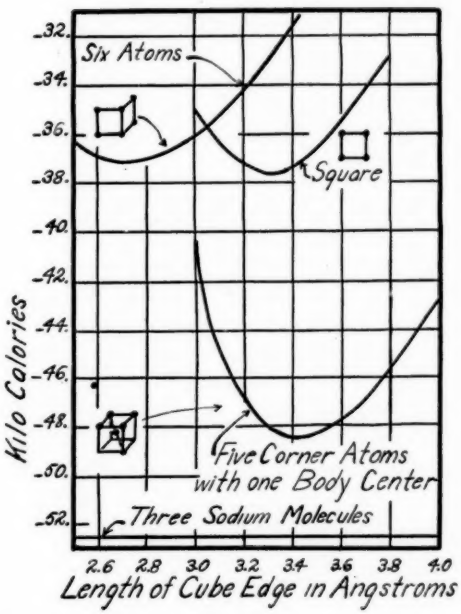


FIG. 3. Binding energies of six atom configurations.

TABLE II.

Configuration	r_0	$E_{min.}$
Molecule	0.76	−101.5
Three atoms in line	0.93	− 90.0
Square	1.0	−117.0
Five atoms at cube corner, sixth at body center	1.3	− 35.7

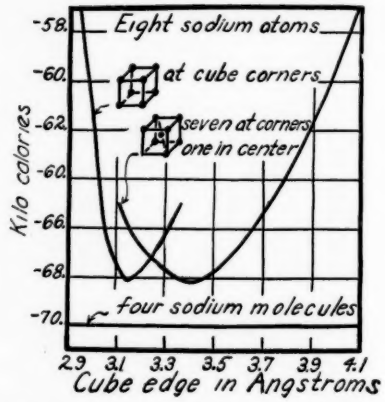


FIG. 4. Binding energies of eight atom configurations.

DISCUSSION

The data presented indicate the manner in which a unit cell would grow from the vapor phase away from surfaces. Fig. 1 shows that, of the possible configurations of four atoms there evaluated, the square configuration is the most stable. This may arise either from four atoms or two molecules, the relative frequency of the two modes of formation being, of course, determined by the pressure-temperature relations. It will also be seen that this configuration of four atoms is more stable than that of two sodium molecules by about 2 kilo.cals. Its concentration, however, under normal conditions, will be vanishingly small. This plane configuration is more stable than any of the possible three-dimensional configurations, as has already been emphasized in another connection by Eyring.[13] Further, as shown by the curves in Fig. 1 for the linear and right-angle configurations, should a linear aggregate of four atoms arise, an activation energy would be required if the mechanism of square formation passed through the right angle configuration shown.

For five atom configurations, Fig. 2, it is noteworthy that all the cases investigated show an inferior degree of stability to the square configuration. In contrast to the case of four atoms, the cube corner configuration is, in this group, the most stable. It is evident, therefore, that, in the cases considered, the approach of a fifth atom to a square can be accomplished with the minimum activation energy when the approach is along the cube edge. The approach of a fifth atom produces, in general, an increase in the edge dimension at the position of maximum stability, most pronounced in the face centered configuration, where the edge is now 4A. It should be noted, however, that, even in this case, the distance of nearest atoms is 2.83A, hence less than that in the diatomic molecule.

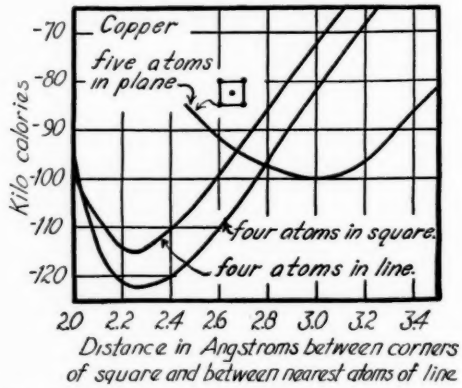


FIG. 5b. Four and five atom configurations of copper, coulombic binding 30 percent of total binding.

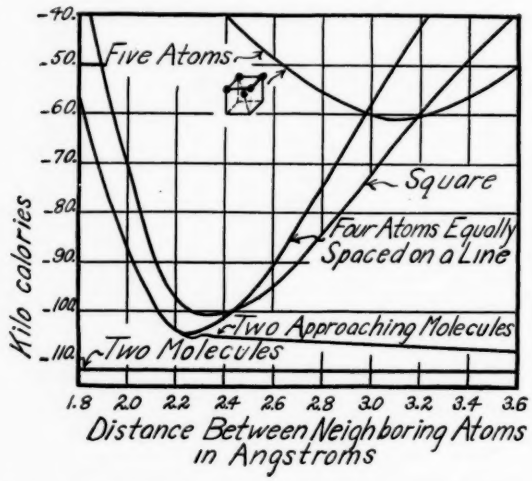


FIG. 5a. Potential energy for configurations of copper atoms when the coulombic is taken as 20 percent of the total binding.

In the case of six atoms, Fig. 3, the striking fact emerges that the cube corner configuration is still less stable than the square configuration. Here, however, the stabilizing influence of the body center atom makes itself very evident. The body center configuration of six atoms is some 10.5 kilo.cals. more stable than the square. Three molecules of sodium are, however, the more stable system by about 4 kilo.cals.

The increased stability obtaining with the body centered configuration is even more pronounced in the case of the eight atom configuration. Here, the addition of two more sodium atoms to the six atom body-centered system decreases the potential energy of the system by a further 20 kilo.cals., a decrease which is greater than the binding energy of the molecule. It will be seen that the binding energy is practically equal to that of four molecules. Fig. 4 shows, however, that this configuration has practically the same binding energy as that of a cube with edge equal to 3.15A units. There is, therefore, the possibility that the body center atom may pass to the eighth cube corner, with an accompanying shrinkage of the lattice dimension. Presumably, a ninth atom would stabilize the body centered configuration. We hope, at a later date, to examine this possibility as an extension of this work.

Summarizing the data on all the configurations concerned, it would seem that the formation of a unit cell would proceed from the atoms, via the diatomic molecule to a square. A fifth atom would add along the cube edge. The sixth would enter the lattice at the body center and the cell would be completed by location of atoms at the remaining cube corners. It may further be emphasized that these several stages will involve definite, if small, activation energies of the order of 2 or 3 large calories at certain points in the synthesis.

We desire next to draw attention to the instability of such a unit cell. As we have seen, the binding energy of the unit cell is approximately equivalent to that of four molecules of sodium. Bulk crystalline sodium is formed from molecular sodium with the evolution of 17.25 kilo.cals. per gram atom (heat of sublimation, $\lambda_{Na}=26$ kilo. cals.; $D_{Na_2}=17.5$ kilo.cals.). One must conclude that, until one reaches structures more complex than the unit cell, the aggregates differ energetically but little from the "twins" visualized by Frenkel[14] as the units of deposited films of the metals, and, statistically, the twin structures would be favored. Our conclusion as to the unit cell is in best agreement with our knowledge of the high vapor pressures, solubility, and the like, of finely divided particles. It also confirms our present concepts of the abnormal activity, energetically, of incompletely crystallized units on surfaces such as are assumed to be of importance in the phenomena of adsorption and surface reactions. It also indicates a possible reason for the marked supersaturation effects shown by certain metallic vapors.

It will be noted that the edge dimension of our best unit cell (cube edge = 3.4A) is still far from the distance required in the crystal lattice (cube edge = 4.3A). The nearest atom distance is 2.95A as compared with 3.15A in the diatomic molecule and 3.7A in the bulk crystal. That expansion, to distances greater than that of the atoms in a diatomic molecule, may occur with arrays of many unit cells is indicated by our data for three and four atom linear configurations which shows a definite expansion of the interatomic distance in the most stable state.

Since the coulombic binding is independent of electron spin it is additive, to the approximation here considered, for a large crystal. We determined the value of these bonds from a central atom outwards over the 82 nearest neighbors and this amounted to -36.7 kilo.cals. An integration to infinity beyond this gave a total coulombic binding of -37.8 kilo.cals. per gram atom. In addition to the attraction due to coulomb forces there is also that due to van der Waals' forces. This we have estimated from the polarizability of sodium atoms. For sodium practically the entire light absorption is that due to the D-lines so that to estimate the van der Waals' forces between atoms, $E=\frac{3}{4}(\alpha^2 h\nu/R^6)$, we may use[18] the polarizability α and the frequency ν corresponding to the D-lines. The second order Stark effect ΔE may be written

$$\Delta E=\sum_i \frac{|X_{0i}|^2}{E_i-E_0} e^2F^2=\tfrac{1}{2}\alpha F^2,$$

where F is the field strength, X_{0i} is the corresponding matrix component for the x coordinate of the electron. But, $\sum_i (E_i-E_0)|X_{0i}|^2=h^2/8\pi^2 m$ as one sees immediately by using the commutation rule $\sum_i (P_{0i}X_{i0}-X_{0i}P_{i0})=h/2\pi i$ and from the fact that $P_{ij}=dX_{ij}/dt=2\pi i m(E_i-E_j)X_{ij}$. For the D-lines, we may neglect the difference in the values of E_i for the different final levels, so that we may write,

[18] F. London, Zeits. f. physik. Chemie **11B**, 222 (1930).

$$E=h^2e^2F^2/(8\pi^2m(E_i-E_0)^2)=\tfrac{1}{2}\alpha F^2,$$

whence,

$$\alpha=e^2h^2/(4\pi^2m(E_i-E_0)^2)=24.7\times10^{-24}\text{ cc},$$

a rather large polarizability. As has already been emphasized for hydrogen atoms by Eisenschitz and London[19] such a value for the polarizability only has significance when applied at distances of the order of kinetic theory diameters or larger. Over such distances the value for the van der Waals' potential between sodium atoms amounts to −1.5 kilo.cals. per gram atom. The combined van der Waals' and coulombic bindings thus amount to −37.8−1.5=−39.3 kilo.cals. Since the heat of sublimation of sodium is 26 kilo.cals. per gram atom it would seem that the interchange energy in the large crystal must be about +13.3 kilo.cals. This represents a positive interchange energy equal numerically to about 36 percent of the coulombic binding. It is of interest to note that in our progression from four atoms to eight the interchange binding has become progressively more positive and in the eight atom case has reached numerically 32 percent of the coulombic binding.

The calculation given refers to van der Waals' forces operative at or beyond distances of 9.37A, and implies a zero value for the binding at lesser distances. If one assumes the van der Waals' attraction operating between atoms at distances less than 9.37A is equal to that at 9.37A, then the total van der Waals' binding amounts to −2.41 kilo.cals. Had the limit of the calculation been set, not at 9.37A but at 4.8A, the van der Waals' energy would amount to −15.2 kilo.cals. With such values for the van der Waals' energy, the interchange energy of a large crystal would be a correspondingly larger numerical fraction of the coulombic-van der Waals' attraction.

With respect to copper, our calculations assume that only one valence electron is operative. The data accumulated add nothing in principle to the conclusions already stated with reference to sodium. The outstanding divergence is in the magnitude of the energy differences between minima. With an assumed 20 percent coulombic binding the energy difference between the square and five atom face center is as much as 40 kilo. cals. With an assumed 30 percent coulombic binding the energy difference is 25 kilo.cals. In either case the contrast with sodium is marked. The crystallization of small aggregates should, therefore, require a higher temperature with copper than with sodium, a quite reasonable conclusion. Fig. 5a shows, in addition, the activation energy of the formation of a linear aggregate of four atoms from a pair of molecules.

The influence exerted by the actual magnitude of the coulombic-interchange ratio is best exhibited by a consideration of the data for hydrogen with a 10 percent coulombic binding. In this case, the square configuration, having a potential energy of −117 kilo.cals., or 86 kilo.cals. greater than that for two hydrogen molecules would require an activation energy of at least 86 kilo. cals. for its formation, obviously impossible of attainment. With larger aggregates of atoms the situation is still more impossible. The binding energy of the six atoms in the body centered configuration is but one-third that of a single hydrogen molecule. The enormous expansion of the lattice caused by the high interchange energy ratio is also to be noted. The data show conclusively why hydrogen cannot form a metallic lattice.

[19] R. Eisenschitz and F. London, Zeits. f. Physik **60**, 491 (1930).

The Thermal Decomposition of Ethyl Mercaptan and Ethyl Sulphide

NELSON R. TRENNER[1] AND H. AUSTIN TAYLOR, *New York University*

(Received October 7, 1932)

The thermal decompositions of ethyl mercaptan and ethyl sulphide have been studied by a static method and shown to proceed homogeneously in glass vessels which have become poisoned by products of reaction. The rate curves of both exhibit an induction period shown to be due to a reaction between ethyl and hydrogen sulphides yielding what appears to be a dimercaptan. The subsequent decomposition of this intermediate is unimolecular but complicated by a reverse reaction. The energies of activation of formation and decomposition of the intermediate are each about 40,000 calories, the rate of formation being slightly greater than the rate of decomposition at temperatures around 400°C. The unimolecular rate falls off below 150 mm which would correspond with six squared terms involved in the activation. No foreign gas has been found to maintain the rate. The existence of a complex equilibrium detracts somewhat from the certainty of interpretation of data and mechanism. A critique of similar recent work substantiates the conclusions here drawn though differing from previous interpretations.

THE paucity of accurate data on organic sulphur compounds would alone justify the present study, but in addition the constant literature references to the analogies existing between these sulphur compounds and the corresponding oxygen derivatives, would suggest a simplicity of decomposition mechanism which might be useful at the present time in its bearing on the kinetics of reaction in general. It has frequently been suggested[2] that the aliphatic mercaptans behave thermally in a manner similar to the amines and might therefore be suspected of decomposing in a unimolecular manner. In fact this is the supposed finding of Malisoff and Marks recently for propyl, butyl, amyl and heptyl mercaptans, both iso and normal. That the sulphur compounds should differ from their oxygen and nitrogen analogs due to the relative ease with which they may be converted from one valence type to another seems to have been continually overlooked. Partly on this account and partly also on account of the methods employed which have usually been dynamic in character, the earlier conclusions regarding the mechanism of mercaptan decomposition are erroneous. This paper will show that the reaction is far from being a simple disruption into hydrogen sulphide and an unsaturated hydrocarbon but involves a series of consecutive reactions, one of which appears to be unimolecular, complicated by the existence of an equilibrium in which polysulphides seem to play an important part. That the reaction is not simple was immediately shown by the first static determination, in the existence of an induction period in the decomposition rate and only by elucidating the cause of this induction period was the mechanism of the whole reaction realized. The study of this induction period called for an investigation of the kinetics of decomposition of ethyl sulphide. The similarity of mechanism found for the thioether and thioalcohol decompositions necessitates their simultaneous discussion and serves further to differentiate between the sulphur and oxygen analogs. This discussion will be facilitated by a presentation of the experimental data for both compounds beforehand.

ETHYL MERCAPTAN

The experimental procedure for all the static studies made was identical with that previously described in reports from this laboratory.[3] The mercaptan, initially an Eastman sample, was dried for a week over sodium carbonate, fractionated between 34.8° and 35.5°C and refractionated between 35.0° and 35.3°C. This was then sealed under its own vapor pressure to the reaction vessel-manometer system. The rate of change of

[1] Abstract from a thesis presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy at New York University, June 1932.

[2] W. F. Faragher, J. C. Morrell and S. Comay, Ind. Eng. Chem. **20**, 527 (1928); W. M. Malisoff and E. M. Marks, ibid. **23**, 1114 (1931).

[3] H. A. Taylor, J. Phys. Chem. **34**, 2761 (1930) et seq.

pressure with time could then be followed on the mercury manometer in the usual manner.

A few preliminary experiments showed that the course of reaction involved an induction period with an autoaccelerating rate up to a maximum and a subsequent falling off yielding the hysteresis type curves as shown later. It was early observed that although the shape of the rate curve subsequent to the point of inflection was easily reproducible the length of the induction period was quite erratic. It was found however that after three or four experiments had been performed successively the surface of the vessel had become stabilized and results could be duplicated, a duplication which was possible even after some months and in a different reaction chamber. This surface effect is discussed later but necessitated in the work a daily stabilizing of the reaction vessel before reliable results could be obtained.

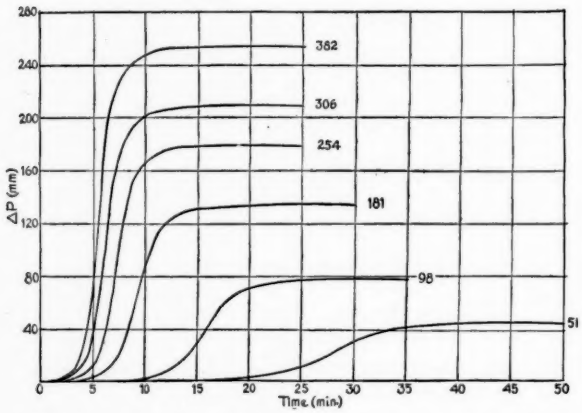


FIG. 1. Curves of the decrease in pressure plotted against time, showing the induction period in the decomposition of ethyl mercaptan at pressures of 51, 98, 181, 254, 306 and 382 mm and at 410°C.

In this manner data were obtained at temperatures from 380°–410°C and at pressures from 50 to 400 mm. Fig. 1 shows a typical set of curves obtained at 410°C. The peculiar behavior of the induction period suggesting a heterogeneous reaction, a rigorous test was made by adding powdered Pyrex glass to the reaction vessel. The first run made after this addition and complete evacuation of the system gave a decomposition rate for the mercaptan with a greatly reduced induction period. In subsequent reactions the period lengthened until eventually the "stable-period" with the empty bulb was reproduced. The fact of an induction period, significant as it so frequently is of chain reactions, suggested a further test for homogeneity by the use of a potassium chloride surface. To this end the surface of the empty reaction bulb was coated with the crystalline salt and the rate of decomposition again measured. Results similar to those with the added glass powder were obtained, the induction period being short initially but lengthening with "ageing" to what may be termed the normal in view of its reproducibility. Fig. 2 shows some of the rate curves obtained with added surface and with potassium chloride, the changing length of the induction period being obvious. It will be observed from these curves, as has been found continuously throughout the work, that at a given temperature and given initial pressure the slope of the curve at the inflection is always the same regardless of the length of the induction period. This constancy must mean that if more than one reaction is involved, the secondary ones are strictly homogeneous under all conditions whilst the primary reaction responsible for the induction period though capable of catalysis by the glass surface becomes eventually homogeneous, possibly through a poisoning of the surface by decomposition products. An inspection of the apparatus showed that the cool connecting tubes to the reaction vessel were gradually darkened by a dark brown or black deposit which would distil off in vacuo on warming, while the reaction vessel kept constantly heated became only slightly

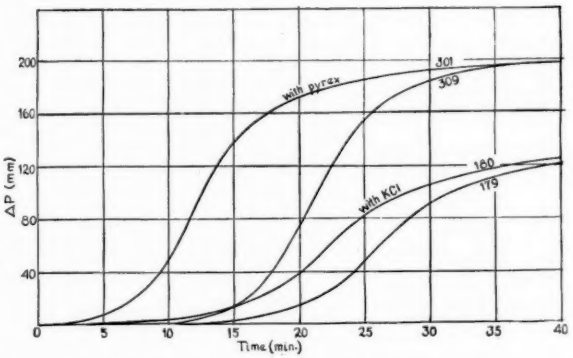


FIG. 2. Rate curves showing the effects of the addition of powdered Pyrex glass (with Pyrex) and potassium chloride (with KCl) to the reaction vessel and two rate curves when no powdered material was added.

darkened. The deposit is certainly not carbon and in all probability is a polysulphide.

On studying the rate curves obtained for different initial pressures at a given temperature, it appeared that the portion of the curves subsequent to the induction period might well represent a unimolecular reaction. The effect of foreign gases was therefore determined. Ten gases including oxygen, nitrogen, hydrogen, carbon dioxide, propylene, ethylene, sulphur dioxide, helium, hydrogen sulphide and ammonia were used with results shown graphically in Fig. 3. In each case, oxygen excepted, 100 mm of the gas was added to 180 mm of the mercaptan vapor. With oxygen only 5 mm were used because of the pronounced effect it had on the induction period. The significance of the order, relative position and slopes of these curves should be noted. Their importance will appear in the later discussion. For the present suffice to note that the secondary portions of the curves all have the same slope, with the exceptions of propylene and ethylene, substantiating the previously suggested unimolecular character of the later reaction.

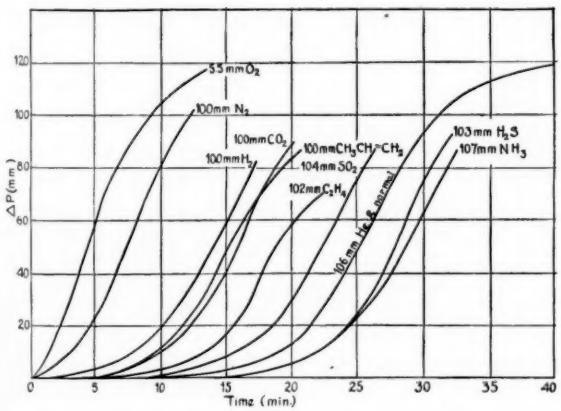


FIG. 3. Rate curves for the decomposition of ethyl mercaptan in the presence of inert gases.

The specific effects of decomposition products were studied by several injection tests made by allowing a certain amount of mercaptan to react until it had reached its maximum rate, that is, the inflection in the rate curve, and then introducing about an equal quantity of fresh reactant whence the rate was followed to the end. Fig. 4 shows the results so obtained in one case. Knowing from previous experiment the shape of the rate curve for the initial sample, had no injection been made (dotted in the diagram and labelled 'normal'), the rate curve for the injected sample may be 'synthesized' as shown by subtraction of the ordinates of the normal curve from those of the 'actual' observed curve. The curve so obtained will be discussed later.

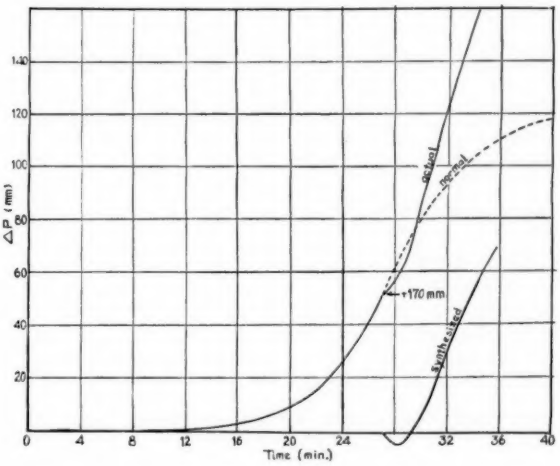


FIG. 4. Rate curve for the decomposition of ethyl mercaptan when an additional sample was added during the course of the experiment. The "normal" curve shows the rate expected, if no addition had been made. The "synthesized" curve is secured by subtracting the ordinates of the "normal" curve from those of the "actual" curve.

The extent of reaction is found to vary with temperature and pressure, a volume increase of from 63 to 76 percent being obtained under varying conditions. That this may represent an equilibrium is qualitatively substantiated by the fact that a higher initial pressure of mercaptan always results in a lower percentage conversion as may be expected for a reaction occurring with a volume increase. Further, a rough calculation from the meagre available data, assuming ethylene and hydrogen sulphide as the final products, shows the decomposition to be endothermal in accord with the observation of a higher percentage conversion at the higher temperatures. As final evidence of an equilibrium, a mixture of 180 mm of ethylene and 190 mm of hydrogen sulphide showed a contraction of 34 percent after twenty-two hours, the reaction appearing to be complete. Such a mixture would correspond to 180 mm of ethyl mercaptan which at the same temperature gave a percentage change of 69.6. With due al-

TABLE I.

Initial press. in mm	Percent decomp.	t_{25}	t_{50} in min.	t_{75}
	Temperature 386°C			
380	63.3	1.54	3.12	5.99
309	64.6	1.57	3.34	6.46
254	66.5	1.49	3.31	6.24
180	69.6	1.80	3.60	6.89
99	76.4	2.98	5.97	8.67
	Temperature 393°C			
383	64.0	1.05	2.20	4.03
311	65.5	1.20	2.53	4.69
254	67.5	1.16	2.38	4.60
	Temperature 400°C			
383	65.0	0.76	1.61	3.00
311	67.2	0.77	1.64	3.25
252	69.0	0.84	1.74	3.25
181	72.2	0.81	1.88	3.60
99	77.1	1.16	2.36	4.32
	Temperature 410°C			
382	66.2	0.57	1.10	1.94
306	68.2	0.54	1.12	2.06
255	70.0	0.58	1.14	2.03
181	73.4	0.54	1.11	2.15
99	78.8	0.58	1.47	2.60
51	84.0	1.10	2.13	3.86

lowance for side reactions as evidenced by the presence of polysulphide these figures are in excellent agreement and significant of an equilibrium in the system. That the later portion of the curve corresponds approximately to a unimolecular reaction may be seen from the values of the quarter, half and three-quarter lives given in Table I. The method of calculating these must be deferred until the mechanism has been presented.

TABLE II.

Temp.	Init. press. P	Inflection Point Time	Press.	Press. unreacted P_I	Ratio P_I/P
386°C	380	17.22	84	296	0.770
	309	20.22	78	231	0.753
	254	22.35	72	182	0.730
	180	25.42	52	128	0.762
393	383	13.02	90	293	0.765
	311	14.70	78	233	0.758
	254	16.00	67	187	0.750
400	383	9.13	93	290	0.758
	311	10.13	79	235	0.754
	252	11.30	62	190	0.768
	180	13.95	58	123	0.712
410	382	5.05	90	292	0.764
	306	5.70	78	228	0.754
	255	6.80	72	183	0.734
	181	9.00	57	124	0.716
	99	15.59	34	65	0.711

At the higher pressures the constancy of the quarter lives is good, while at the lower pressures the time increases. There is a marked drift in the times of 75 percent change which may be due to the fact that the reverse reaction causing the equilibrium has not been fully allowed for. Taking mean values of the quarter lives at the higher pressures the Arrhenius equation yields for the energy of activation a value of 40,100 cals. A similar calculation by using the half-lives gives 41,200 cals.

All the above calculations, as will appear later, are made with reference to the later portion of the rate curve that is after the point of inflection. Attempts to separate the several reactions suspected as occurring by a shift of temperature and pressure proved fruitless since it was found that not only is the temperature coefficient of the induction period and hence of the reaction causing it of the same order as that of the subsequent reaction given above but also the ratio of the amount of reactant undecomposed at the point of inflection to the initial pressure is constant with varying temperature and pressure. Table II will illustrate these facts. Furthermore the energy of activation calculated for the induction period alone is 42,800 cals.

ETHYL SULPHIDE

In numerous instances experimenters have found that pyrolysis of a mercaptan yields the corresponding sulphide as one of the products. Thus Kahn[4] states that octyl mercaptan boiling at 198–200°C decomposes to give octyl sulphide and hydrogen sulphide. For heterogeneous mercaptan decompositions on metallic or metal sulphide surfaces Elgin[5] and Sabatier and Maihle[6] found sulphide formation. If this were the general procedure one could easily account for the induction period in the mercaptan decomposition since the formation of a molecule of ethyl sulphide together with a molecule of hydrogen sulphide from two molecules of mercaptan would involve no volume change. The observed volume increase might be due to subsequent decomposition of the ethyl sulphide into ethylene and more hydrogen sulphide. For this to be satisfactory however

[4] Kahn, Bull. Soc. Chim. Roumania **5**, 70 (1923).
[5] J. C. Elgin, Ind. Eng. Chem. **22**, 1290 (1930).
[6] Maihle, Comptes Rendus **150**, 1569 (1910).

ethyl sulphide should show no induction period on decomposition. It was originally in an effort to test this that the ethyl sulphide study was made.

The ethyl sulphide used was an Eastman sample dried over sodium hydroxide and twice fractionated, the fraction employed boiling between 90.8 and 91.6°C at 765.7 mm pressure. The apparatus used was the same as for the mercaptan save that to prevent condensation of the sulphide the capillary tubes outside the furnace were maintained at 100°C by auxiliary heaters. The course of the reaction however contrary to the suggested expectation did involve an induction period and seemed to parallel in almost every detail the mercaptan results suggesting a similarity of mechanism for both decompositions. This similarity was reflected in the effects of increased surface and of added gases as also in the existence of an equilibrium.

The effect of increased surface was precisely as found for the mercaptan, namely, a shortened induction period initially, gradually lengthening to the normal rate as in the empty reaction vessel. As regards the equilibrium, assuming one mole of the thioether to give two of ethylene and one of hydrogen sulphide, there should be a 200 percent change observed. Actually only 112 to 124 percent under varying conditions was found indicating a reaction from 55 to 62 percent complete. These values are considerably lower than for mercaptan but should not be unexpected if an equilibrium exists, in view of the higher ethylene concentration from the thioether as compared with that from mercaptan. As confirmation of this 357 mm of ethylene and 182 mm of hydrogen sulphide were allowed to react at 420°C, and on completion of reaction after twenty-two hours had contracted 24 percent. This, calculated as an equivalent amount of thioether decomposing would correspond to 63.3 percent while the actual observed change for 181 mm of thioether was 62.2 percent, an obvious agreement. Finally with reference to the foreign gases, with one exception, hydrogen sulphide, their effects on the sulphide were precisely similar to those on the mercaptan. With hydrogen sulphide, whereas the induction period of the mercaptan was actually increased, that of the thioether was almost completely removed. It seemed probable that the two reacted together rapidly to yield a product which underwent a steady decomposition thereby removing the induction period. This system therefore was made the subject of a special study as is seen later.

TABLE III.

Init. press. (mm)	Percent decomp.	t_{25}	t_{50} (mins.)	t_{75}
	Temperature 393°C			
303	56.0	1.76	3.83	7.29
246	57.9	1.87	4.00	7.48
	Temperature 400°C			
304	57.3	1.34	2.76	5.21
253	57.6	1.35	2.94	5.50
180	61.9	1.69	3.64	6.75
	Temperature 410°C			
301	58.0	0.84	1.76	3.16
251	59.1	0.91	1.94	3.50
178	61.1	0.95	2.09	3.86
	Temperature 420°C			
301	59.1	0.54	1.10	1.90
263	59.6	0.49	1.13	2.06
181	62.0	0.63	1.35	2.50

Tables III and IV give the salient data for the thioether paralleling those for mercaptan.

The data in Table III are as in the mercaptan case relative to the rates after the induction period. The constancy of quarter lives is again evident, the values yielding an energy of activation of 43,800 calories. The half lives give 42,700 calories whilst the induction period itself gives 43,000 calories. The ratios in Table IV are again seen to be constant although the value is higher than for mercaptan. This is due no doubt to the slightly longer induction period for thioether than for mercaptan. The succeeding rate for thioether is also less than for mercaptan as might be anticipated, the higher ethylene concentration acceler-

TABLE IV.

Temp.	Init. press. P	Inflec. press.	Press. unreacted P_I	Ratio P_I/P
393	303	46	257	0.848
	246	39	210	0.854
	183	34	149	0.814
400	304	48	256	0.846
	253	43	210	0.830
	180	33	147	0.816
410	301	46	255	0.848
	251	40	211	0.840
	178	38	141	0.792
420	301	50	257	0.834
	263	46	217	0.826
	181	40	141	0.780

ating the reverse reaction indicated by the percentage decompositions shown in Table III. This constancy of the amount decomposed at the point of inflection with varying temperature and pressure again precludes the possibility of separating the reaction into its constituents.

Ethyl Sulphide and Hydrogen Sulphide

The behavior of this system as already mentioned was suggestive that the primary reaction with the ethyl sulphide alone is enormously accelerated in presence of hydrogen sulphide, an acceleration which since it did not occur with the mercaptan is probably due therefore to specific chemical reaction between the ethyl and hydrogen sulphides. It seemed possible that this reaction might be giving rise to a compound which was actually the intermediate, decomposing unimolecularly in both the mercaptan and sulphide cases. If this is true then a study of the velocity and energy of activation should give results in substantial agreement with those already found for the secondary reactions, subsequent that is, to the induction period.

In the experiments made, equivalent quantities of the ethyl and hydrogen sulphides were used. Fig. 5 illustrates the course of the reaction at 386°C the lowest temperature studied.

The induction period has almost entirely disappeared. Even in the worst case at 127 mm a slight induction may be seen but amounts to no more than one minute as compared with the twenty minutes for thioether alone. Added hydrogen even when present in an amount three times

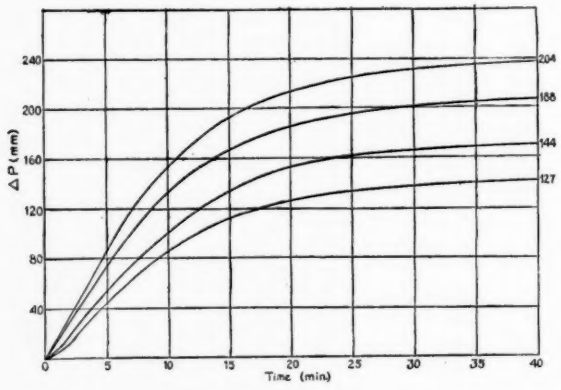


Fig. 5. Rate curves for the decomposition of ethyl sulphide in the presence of hydrogen sulphide.

Table V.

Init. press.	Percent decomp.	t_{25}	t_{50}
	Temperature 386°C		
402	59.4	3.00	6.53
355	60.0	3.00	6.75
291	60.3	3.24	7.16
252	58.8	3.24	7.25
	Temperature 393°C		
399	57.9	2.07	4.52
353	59.4	2.25	4.95
305	60.5	2.50	5.20
	Temperature 410°C		
402	58.4	0.98	2.08
350	59.3	1.07	2.30
309	61.8	1.06	2.39
252	60.6	1.16	2.58

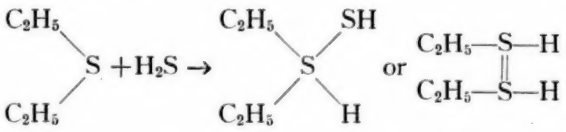
the total reactants was found to be without effect, irrespective also of the initial pressure of reactant. The same was found true of air although here a slight shift of end point was observed possibly due to some oxidation.

In Table V are given the values of the fractional lives showing a constancy indicative of a unimolecular rate. The percentage decompositions are included for comparison. At a pressure of about 300 mm at 410°C the mercaptan changes by 68.2 percent, the ethyl sulphide-hydrogen sulphide by 60.4 (calculated from 150 mm of each) and the pure ethyl sulphide by 57.8 percent. The order of these results clearly indicates the influence of excess of either hydrogen sulphide or of ethylene. The energy of activation calculated from the above data gives an average value of 39,500 calories in good agreement with the value of 40,500 found for the mercaptan.

Discussion of Mechanism

The presence of the induction period in the decomposition rate of both the mercaptan and sulphide is to be taken as suggesting the formation of some intermediate, either with no volume change or with a volume decrease, which subsequently decomposes with a volume increase. From the constancy of the energies of activation of both the induction periods and the subsequent rates, from the similar influence of inert gases and lastly from the constant characteristics of the observed end points it is probable that the same intermediate is formed in both cases. Since this induction period for the sulphide is removed in

presence of hydrogen sulphide the intermediate would appear to be formed from them in some such way as:



Subsequent decomposition of this latter into ethylene and hydrogen sulphide would yield the observed overall volume increase. The formation of polysulphides which are actually found might be accounted for by a decomposition of the intermediate into disulphide. Unpublished work in this laboratory shows that the disulphides are much less stable than mercaptan or thioether and furthermore are capable of combining with free sulphur to give polysulphides.[7] The decomposition of the mercaptan would entail therefore a primary split into sulphide and hydrogen sulphide which would react together as above, accounting for the absence of effect of added hydrogen sulphide on the induction period of the mercaptan since sufficient hydrogen sulphide is already present from the primary reaction.

In confirmation of this suggestion for the intermediate it may be noted that addition reactions to alkyl sulphides are well known. In particular Moelwyn-Hughes[8] attempting to show that the unimolecular decomposition of triethyl-sulphonium bromide in solution would parallel that in the gas phase, points out that the energy of activation of the combination of ethyl sulphide and ethyl bromide varies from 39,600 to 43,400 calories depending on the solution. The activation energy of the induction period of ethyl sulphide is here found as 43,000 calories an agreement which may well be expected since essentially the same types of bonds are involved in both cases.

If this mechanism be accepted, the secondary reactions, subsequent that is, to the induction period and previously spoken of as being unimolecular, should correspond with the decomposition of the intermediate. The actual velocity constants of these secondary reactions in both mercaptan and sulphide cases should agree with those for the ethyl sulphide-hydrogen sulphide reaction. It has been shown in Tables II and IV that the ratio of the amount decomposed at the point of inflection to the amount initially present is constant with varying temperature and pressure for both the mercaptan and the sulphide. This constancy is not impaired by the presence of those gases which may truly be considered as inert as Table VI will show, where values of the ratio are given for mercaptan in presence of various gases at 386°C. It should be noted in the above that the nitrogen employed was later shown to be impure, containing oxygen which as was found had an enormous influence on the reaction rate probably due[9] to the formation of disulphide. Further, ethylene and similarly propylene, being a reactant yields a ratio which is high but which is closely approximate to the value found in the thioether runs.

TABLE VI.

Added gas	Init. press. P	Inflection point Time	Inflection point Press.	Press. unreacted P_I	Ratio P_I/P
None	180	25.4	52	128	0.762
N_2	198	6.95	44	154	0.778
H_2	181	13.4	44	137	0.757
C_3H_6	182	13.8	35	147	0.808
CO_2	184	15.5	46	138	0.750
C_2H_4	179	16.5	27	152	0.850
SO_2	174	21.8	44	130	0.747
He	178	24.8	46	132	0.742
H_2S	188	27.4	45	143	0.760
NH_3	186	28.5	47	139	0.748

This constancy clearly demonstrates that the temperature coefficient of the reactions before and after the point of inflection must be essentially the same, that the overall rate up to the point of inflection is approximately proportional to the initial pressure and that the concentration of intermediate at the inflection point is independent of the length of the induction period for the same temperature and pressure. In other

[7] 10 g of sulphur were sealed with 15 g ethyl disulphide in a tube and heated for 24 hours at 135°C. The sulphur went into solution but failed to precipitate on cooling. The orange colored liquid formed, boiled over a range from 140° to 195°C with no definite halts and left an almost black residue. A check with pure disulphide alone after similar heating boiled over a range of only 149.5–150.5°C.

[8] E. A. Moelwyn-Hughes, Chem. Reviews **10**, 248 (1932).

[9] *Schmidt's Organic Chemistry*, 1st Ed., p. 122 (1927). Beilstein, 4th Ed., **1**, 347 (1918).

words the points of inflection on any of the rate curves are comparable points and fractional lives and velocity constants may be calculated from these as a zero time. It is in this way that the previously quoted values were obtained. A further correction has been applied since the end-points at the various temperatures and pressures are variable. In the absence of an exact knowledge of the equilibrium or the actual velocities of the reverse reactions, the end-point of the reaction at the highest pressure for any temperature was taken as a standard and all others compared with it by multiplying their fractional lives by the ratio of the high to low pressure end-points. The correction is not precise but since the change involved is small in any case it was not deemed necessary to elaborate it. The location of the point of inflection was obtained from large plots of the reaction rate curves. On this basis velocity constants were calculated for the secondary reaction, the unimolecular rate, for both the mercaptan and thioether. In Table VII are included for comparison velocity constants for the thioether-hydrogen sulphide reaction calculated directly from observed data. Examination of the

TABLE VII. *Velocity constants at 393°C.*

Ethyl Mercaptan		Ethyl Sulphide-Hydrogen Sulphide		Ethyl Sulphide	
Init. press. 383 mm Time in mins.	Inflection press. 293 mm k	Init. press. 399 mm Time in mins.	k	Init. press. 302.5 mm Time in mins.	Inflection press. 255.5 mm k
0.5	0.120	1	0.0714	1	0.0359
1.0	0.135	2	0.0695	2	0.0364
1.5	0.139	3	0.0705	3	0.0376
2.0	0.139	4	0.0715	4	0.0385
3.0	0.133	5	0.0688	5	0.0392
4.0	0.122	6	0.0664	6	0.0401
5.0	0.111	7	0.0646	10	0.0440
		8	0.0627		

constants given as also for those at other temperatures and pressures shows a slight increase for about one and a half minutes, a constancy, and then a falling off. This falling off may be due to the decreased concentration of reactant as in many unimolecular reactions or to complexities caused by the reverse reactions. The preliminary increase appears to suggest that at the point of inflection the primary reactions are not quite complete, but go on building up the concentration of intermediate, since true constancy is invariably reached only after the first minute and a half after the inflection point. At this point of constancy of the velocity constants then the concentration of the intermediate is at least approximately known and should permit the evaluation of the rate of the primary reaction.

Consider the following scheme:

$$2A \xrightarrow{k_1} B \xrightarrow{k_2} 4C,$$

which could represent equivalent amounts of thioether and hydrogen sulphide combining to give the intermediate which then decomposes into ethylene and hydrogen sulphide. Starting with a mols of A and leaving x mols remaining after time t the rate of disappearance of A is given by $-dx/dt=k_1x^2$ or $x=a/(1+ak_1t)$. Letting $\alpha=k_1/k_2$, $x=a/(1+ak_2\alpha t)$ or $\alpha=(a-x)/ak_2tx$. Taking as values of k_2 the velocity constants previously calculated, for x the difference between the initial pressure and the amount reacted up to the inflection point and expressing these in moles per liter the values of α vary only from 21 to 25 for all the data observed for the mercaptan and from 44 to 47 for the thioether. By taking the data for the thioether-hydrogen sulphide system at the lowest temperature and pressure where an induction period, though slight, does exist, a calculation similar to the above gives for α a value of 91. Too much faith cannot be placed in these actual numerical values, suffice that the order of magnitude of all is the same, whence it is concluded that the primary split of the mercaptan or of the thioether and the combination of thioether and hydrogen sulphide occur at rates only slightly faster than the unimolecular decomposition of the intermediate. Since the first reaction involves a pressure decrease while the subsequent unimolecular reaction results in a larger pressure increase, the observed induction period must be due to a slight actual, though unobservable, pressure decrease by the first reaction before the concentration of intermediate is sufficient for the second reaction to become appreciable. An initial pressure decrease is actually found in the injection tests shown in Fig. 4. Now the injection of fresh mercaptan was made at the point of inflection of the rate curve of the initial mercaptan, at

which point, as is shown, the concentration of intermediate is at a maximum. The intermediate, being the result of a bimolecular association, will when formed behave as a quasi-molecule. A stabilization on collision with a mercaptan molecule would result in an increased activation rate for mercaptan and hence an increased rate of formation of intermediate with its resultant pressure decrease.

Turning again to the data in Table I, the values of the fractional lives at all temperatures appear to increase as the pressure falls below 150 mm. If this decrease in rate is truly that to be expected for the deviation of unimolecular reactions with decreasing pressures, an approximate measure of the number of squared terms involved in the activation process may be obtained. The calculation being made in the approximate manner of Hinshelwood[10] gives a value of 6 for the number of squared terms. The inability of added gases, particularly hydrogen, to increase the rate at lower pressures recalls the somewhat similar study on the decomposition of ethylene oxide,[11] a reaction also involving an induction period and where the effect of inert gases was somewhat erratic, hydrogen in particular having a marked retarding effect. It is interesting to note that in the mercaptan case the effectiveness with which the various gases reduced the induction period is precisely that found for their effectiveness in quenching mercury fluorescence,[12] which suggests that their action in reducing the induction period may lie in deactivating the nascent intermediate, preventing its dissociation into the original reactants which formed it. Although the necessity for this would not seem great owing to the complexity of the postulated intermediate, the results of the injection tests shown in Fig. 4, where the induction period of the second quantity of mercaptan added was considerably shorter than that of the first, would point in the same direction.

In an endeavor to isolate and study the suspected intermediate several dynamic experiments were made. Since, as has been shown, a maximum concentration of the intermediate is found in the neighborhood of the point of inflection, the conditions of the dynamics runs were chosen to duplicate these. Ethyl mercaptan vapor was drawn through a tube maintained at a suitable temperature in a furnace, at a rate controlled by a capillary to give a time of contact corresponding to the inflection point in the static experiments. The issuing gases passed through a cooling tube at −15°C, where the tarry materials or higher polysulphides condensed, and thence into a carbon dioxide-toluene freezer where all but the fixed gases were removed. After some time the carbon-dioxide freezer was examined and found to contain a light lemon yellow liquid and a white solid which quickly melted on warming, dissolving in the liquid. Examination showed they were neither ethyl mercaptan nor ethyl sulphide. When washed with sodium hydroxide the liquid went into solution, indicating its acidic properties, and on acidification yielded back the yellow liquid. The liquid had a somewhat pleasant though acroleic penetrating odor. It certainly did not possess any of the characteristically disgusting odors of the mercaptans or sulphides. Efforts to purify it by extraction with ether and vacuum distillation were only partially successful.

A similar procedure with ethyl sulphide gave small amounts of the same yellow liquid along with unchanged sulphide. When hydrogen sulphide and ethyl sulphide were used practically no unchanged ethyl sulphide was found though still only small amounts (less than half a cubic centimeter in eight hours) of the intermediate. This latter fact suggests that the induction period in the thioether is partly due to the necessity of some of it decomposing to give hydrogen sulphide before the intermediate can be formed.

The cause of the small yields of intermediate appears to lie in the fact as previously shown that its rate of formation is only slightly faster than its rate of decomposition. By working at much lower temperatures and high pressure (150 atmos.), sufficient was obtained to allow an analysis to be made. A steel bomb was partly filled with 25 cc ethyl sulphide and 25 cc of liquid hydrogen sulphide in a carbon dioxide freezing bath. The bomb was sealed and raised in temperature to 270°C, being maintained there for 56 hours, a period found to give the best yields without ex-

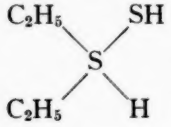
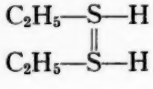
[10] Hinshelwood, *Kinetics of Chemical Change*, p. 126 (1929).

[11] W. W. Heckert and E. Mack, Jr., J. Am. Chem. Soc. 51, 2706 (1931).

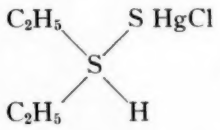
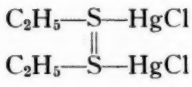
[12] Kistiakowsky, *Photochemical Processes*, p. 126 (1928).

cessive polysulphide formation. The bomb was then cooled in carbon dioxide, opened, allowed to warm up to room temperature removing thereby excess hydrogen sulphide and the remaining light yellow liquid treated with 30 percent caustic soda to separate the mercaptans or intermediate from unreacted sulphide and polysulphides. This solution, after washing with ether to remove mechanically held mother liquor, was then frozen in carbon dioxide and cold dilute sulphuric acid added to liberate again the acid constituents. The necessity for carrying this out in the cold is due to the fact that decomposition of the intermediate is considerably hastened by the presence of an acid, as frequent loss of the product at this stage unfortunately proved. The light yellow liquid was taken up in ether and by addition of mercuric chloride converted into the mercury addition salt which is insoluble in ether and had a light buff color. The yield of the salt was about three grams. The free intermediate could then be obtained by warming the salt in an atmosphere of hydrogen sulphide, forming mercuric sulphide, hydrogen chloride and free intermediate. The sample so obtained was still impure, having a decided mercaptan odor. That it was not mercaptan was shown by its boiling point from 48 to 49.5°C. In fact there seems to be no chemical means of separating this compound from mercaptan.

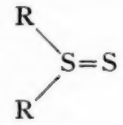
An analysis by the Carius method for sulphur as barium sulphate and chlorine as silver chloride proved totally impossible in presence of the mercuric ion, precipitation of both, especially silver chloride, being incomplete. However by treating the solution from the Carius combustion when only slightly acid with magnesium turnings both silver and mercury may be replaced and the resultant solution analyzed in the usual manner, first for sulphate with barium nitrate and then for chloride with silver nitrate. The mercury analysis is made by weighing mercuric sulphide left after treatment of the mercury salt of the intermediate with hydrogen sulphide at 100°C. The analyses made gave for mercury 69.56, sulphur 11.79 and chlorine 10.88 percent. Taking the earlier suggestions for the intermediate, namely:

I  and II 

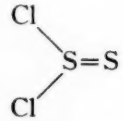
Addition compounds with mercuric chloride would probably yield

I  and II 

Calculated analyses for these two give for I, Hg 55.90, S 18.10 and Cl 9.98 percent, and for II, Hg 67.50, S 10.80 and Cl 11.80 percent. The observed analysis is obviously in better agreement with the second formula, the divergence being undoubtedly due to impurities in the sample obtained. There is however always the possibility that the addition salt in I might also involve two HgCl groups though the second —S—H is hardly a true mercaptan grouping. If this were so, no difference could be noted between the possibilities. It will be observed, too, that the results calculated for case II are precisely those one would obtain for ethyl mercaptan but the intermediate is certainly not mercaptan as judged by its boiling point and other characteristics if not by its odor. In view of the uncertainties on the structure of even the disulphides it seems futile to attempt any further elaboration save to mention the possibility of both. Naik[13] for example presents evidence for dithioethers of structure



suggesting a dual character for sulphur monochloride as Cl—S—S—Cl or



depending upon the polar conditions.

The following reactions therefore appear to have been established:

$$2C_2H_5SH \longrightarrow (C_2H_5)_2S+H_2S$$

$$(C_2H_5)_2S+H_2S \longrightarrow (C_2H_5)_2S_2H_2$$

As to the subsequent reactions all that may be

[13] K. G. Naik, J. Chem. Soc. **119**, 379, 1231 (1921).

said is that hydrogen sulphide and ethylene are present in large quantities along with polysulphides. It is difficult to say whether the intermediate breaks up in the main directly into hydrogen sulphide and ethylene with polysulphides as only a secondary reaction, or whether first disulphide and hydrogen are formed, the disulphide rapidly decomposing as we have found into ethylene, hydrogen sulphide and free sulphur from which innumerable possibilities suggest themselves for polysulphide formation. Suffice to say that we have shown that ethylene and hydrogen sulphide will react together on heating to give mercaptan and the intermediate, which under the experimental conditions opens up all the above possibilities, yielding the highly complex equilibrium spoken of throughout the paper.

In conclusion it may be well to consider somewhat briefly the foregoing in comparison with recent similar work, particularly that by Malisoff and Marks,[14] who find no evidence of any intermediary stages in the reaction mechanism. At the outset their assumption that "no drastic extraneous effect was introduced by the presence of solvent vapors" is open to serious question since as here shown inert gases do markedly affect the induction period, and where unsaturated hydrocarbons are present, the subsequent rate is also changed. They do in fact observe this result with benzene and suggest for it a 'promoter action.' Admitting that the higher homologs are slightly less stable the induction period at 425°C in the presence of an inert gas, which tends to reduce it further, must be small, probably less than a minute. An exposure time of 50 seconds, then, would carry well into the subsequent reactions, though for 10 seconds there should be little if any reaction. This is precisely what they find, namely no reaction of amyl mercaptan at 425° after 9 seconds contact time. They speak further of a range sensitive to the time of exposure occurring at about 52 seconds which from the present work would seem to correspond to the point of inflection. Although, therefore, no induction period was mentioned by them, internal evidence would suggest it. With regard to the effect of foreign gases it is hardly surprising that Malisoff and Marks should find no effect from hydrogen and carbon dioxide since the latter serve only to replace a small amount of the solvent vapors already present to an extent of 6.5 times the reactant.

The absence of any intermediary stages in mercaptan decomposition is judged by Malisoff and Marks from the constancy of the ratio of the amount of mercaptan decomposed to hydrogen sulphide produced. Such a conclusion is hardly justifiable where the intermediate, as has been shown, reacts analytically as a mercaptan. The fact that in the majority of their results the amounts of hydrogen sulphide produced exceed the amounts of mercaptan decomposed indicates serious analytical error as is shown also by their tests for homogeneity where, on an increased surface, a longer contact time gave a smaller percentage decomposition. It is difficult also to understand how with an admitted accuracy of ± 2 percent in mercaptan estimation they state that the mercaptan formed from amylene and hydrogen sulphide was less than 0.001 percent. The temperature coefficient which they find of 1.38 for amyl mercaptan is considerably lower than is found here for the ethyl derivative as also for propyl mercaptan at present under investigation. From their paper this would appear to be due to unjustifiable averaging of numerous erratic results. The parallelism of their temperature coefficient plots is difficult to see and the fact that they are actually straight lines is open to question since but two points are given on each.

In view of these criticisms it would not be justifiable to accept their conclusions that mercaptan decomposition involves a straight split into olefine and hydrogen sulphide in a manner satisfactorily accounted for by a single unimolecular rate.

The main conclusions then to be drawn from the paper are:

1. Decompositions of ethyl mercaptan and ethyl sulphide show a marked parallelism involving the same intermediate and proceeding to the same equilibrium, which is highly complex.
2. The intermediate has been isolated and shows the properties of a mercaptan but with

[14] W. M. Malisoff and E. M. Marks, Ind. Eng. Chem. 23, 1114 (1931).

physical characteristics that differentiate it from any so far described.

3. The intermediate decomposes unimolecularly with an energy of activation of about 40,000 calories at a rate only slightly less than its rate of formation from ethyl sulphide and hydrogen sulphide.

4. Analogies between sulphur and oxygen compounds are liable to be erroneous unless due account is taken of the possible multivalence of sulphur. This has been discussed in connection with recent incorrect suggestions on the mechanism of mercaptan decomposition.

The Influence of Ionization on the Ignition Temperature of Combustible Gases[1]

BERNARD LEWIS[2] AND C. D. KREUTZ,[3] *Pittsburgh Experiment Station of the U. S. Bureau of Mines at Pittsburgh, Pa.*

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The ignition temperatures of methane-"air" mixtures were investigated in a flow system as follows: (1) The spontaneous ignition temperature due to temperature alone was determined. (2) One of the inert gases was passed through a condensed discharge before joining the combustible gas and the change in ignition temperature noted. The individual gases were preheated to 500°C before mixing in the ignition tube which could be heated to any desired higher temperature. Ignition always occurred about 50 cm downstream from the spark chamber. The temperature at which the mixtures ignited was lower when pre-sparking was employed. The gases subjected to the spark were A, He, N_2, O_2. The difference between the spontaneous and pre-sparking ignition temperatures increased in the order named, being about 28°C for A and about 240°C for oxygen under the conditions of this investigation for a final mixture of 8 percent methane in "air" (ratio of oxygen to inert gas in final mixture being the same as in air). A post ignition phenomenon is described which is brought about by delaying the flow of the sparked oxygen for some time after cessation of the spark and then resuming the flow. Such delay times of 2½ minutes were observed. The species which cause ignition possess a long life and are rather easily removed by metal screens. It is shown that the results cannot be accounted for by nitric oxide, ozone, active nitrogen or active oxygen. It is concluded that *electrically charged species or ions are responsible for the lowered ignition temperatures.* A tentative explanation of the results is suggested. It is pointed out that in the ignition of combustible gas mixtures by direct action of a spark, the ions formed in the path of the spark, as well as the thermal energy liberated, play a responsible part in the ignition process.

INTRODUCTION

IT has been known for more than a century that flames and the gases which issue from them are conductors of electricity. The conductors are believed to be both positive and negative ions.[4]

That these charged species, and perhaps more particularly the positive ions, play a rôle in the maintenance and propagation of a flame may be inferred from a number of investigations.[5] One recognizes that the propagation of flame may not take place exclusively through the agency of these charged species. Indeed recent work in this laboratory and elsewhere assures one of the complexity of flame-front phenomena. It is very probable that other active bodies such as energy-rich molecules (uncharged) or some transitory intermediate compound or atom, play a responsible part in the propagation of flame. Moreover, no theory of the flame front can be complete without a consideration of the kinetic problem involved.

As an approach to the general problem, it seemed of special interest to ascertain the effect on the ignition temperature, of introducing electrically charged gases into a combustible gas mixture. This paper contains some preliminary results of such an investigation.

METHOD

It is purposed to produce the ions in one of the inert gases prior to mixing the latter with the combustible gas and to observe their effect on the ignition temperature of the resulting mixture. Of the means available for the production of ions, such as thermal excitation, x-ray and radioactive products, photoionization and the condensed

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[2] Physical chemist, U. S. Bureau of Mines, Pittsburgh Experiment Station, Pittsburgh, Pa.

[3] Research fellow, Carnegie Institute of Technology, Pittsburgh, Pa.

[4] H. A. Wilson, *Electrical Conductivity of Flames*, Rev. Mod. Phys. **3**, 156 (1931).

[5] Malinowski, J. Chim. Phys. **21**, 469 (1924). Malinowski and Lawrow, Zeits. f. Physik **59**, 690 (1930). Bernackyj and Retaniw, Ukv. Physik. Abhand **II**, (1), 9 (1928). F. Haber, Sitzb. preuss. Akad. Wiss. No. 11, 162 (1929). Finch and Cowen, Proc. Roy. Soc. **A116**, 329 (1927). Finch and Thompson, Proc. Roy. Soc. **A134**, 343 (1931). Thornton, Phil. Mag. **9**, 260 (1930). Guénault and Wheeler, J. Chem. Soc. 195, (1931). Bernard Lewis, J. Am. Chem. Soc. **53**, 1304 (1931). H. Muendel, Thesis, Carnegie Institute of Technology, 1931.

electric spark, the latter is clearly the most potent agency. To preserve the ion concentration the following observations are of value. (1) The coefficient of recombination of ions decreases with increasing temperature. (2) The coefficient of recombination of ions reaches a maximum at a certain pressure. For air this maximum is at about two atmospheres. (3) The shorter the time between the production of ions and mixing, the higher the ion concentration.

Materials

The following are the gases and their compositions which were passed through the spark discharge:

Commercial oxygen,	99.5 percent O_2; Ca 0.5 percent N_2;
Electrolytic oxygen,	99.8–9 percent O_2; Ca 0.1 percent H_2;
Oxygen (by $KMnO_4$ decomposition),	99.9 percent O_2;
Nitrogen,	Ca 99.8 percent N_2; Ca 0.2 percent O_2;
Helium,	98 percent He; rest mainly N_2;
Argon,	97.8 percent A, 2.1 percent N_2, 0.1 percent O_2.

The combustible gas was methane. It had the following composition: CH_4, 97.8 percent; C_2H_6, 1.4 percent; C_3H_8, 0.1 percent; C_4H_{10}, 0.1 percent; N_2, 0.6 percent.

The electrodes used were nickel, stainless steel, aluminum, and carbon rods about 6 mm in diameter. The majority of the data were obtained with nickel electrodes.

Apparatus and Procedure

Several apparatuses were constructed. The final one is described below and illustrated in Fig. 1. It was made of Pyrex glass with the exception of the outlet tube *b*, which was of transparent quartz. A quartz-Pyrex graded seal connected the glass and quartz sections. Ignitions took place in the quartz tube *b*. The spark chamber, *m*, was a 6 cm bulb. Its outlet tube was constricted to 4 mm to preserve a high gas velocity, thus eliminating back diffusion of gases. Methane always entered through *e*, the gas to be sparked through *g* and the other gas comprising the mixture through *f*.

The ignition tube *b* had a narrow slit through the furnace insulation for the purpose of observing the ignition and the subsequent movement of the flame. Temperatures were read with platinum-rhodium thermocouples at the mouth of tubes *e* and *f*, at the mixing point and at the wall of the tube where ignition occurred. The furnace was wound in such a way that there was an increasing temperature gradient from *d* reaching a maximum at the ignition point. The latter could be regulated up to 1000°C whereas the temperature of the gases at *d* was 500°C. The individual gases were preheated to 500°C before mixing.

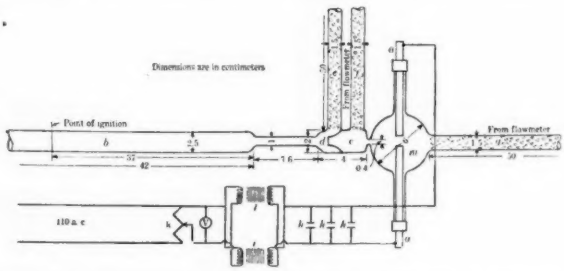

Fig. 1. Apparatus for the study of the effect of ions on ignition temperature.

The ignition was plainly visible. It occurred at the point indicated in Fig. 1, about 50 cm from the spark, whether the thermocouple was present or not. Once formed, the flame always travelled rapidly to the point *d*, where it remained stationary.

The spark discharge circuit consisted of a slide wire resistance used as a potentiometer, a voltmeter across the primaries of two 15,000-volt transformers connected in parallel and three 0.004 m.f.d. condensers, all of which were in parallel with the spark gap. The width of the spark gap was about 1 cm.

The gases were passed separately through calibrated flow meters to produce the desired mixture. Before entering the spark chamber the gas was dried by passage through $CaCl_2$ and P_2O_5 tubes. When nitrogen, helium, or argon was sparked, traces of oxygen were first removed by bubbling through a long tube filled with basic pyrogallol solution. Traces of hydrogen were removed from the electrolytic oxygen by passage over hot platinized asbestos, after which the gas

was dried. When oxygen was sparked, nitrogen was passed through tube *f*; when nitrogen, helium, or argon was sparked, oxygen was passed through tube *f*. For purpose of comparison the three oxygen samples were treated in the same way. The proportion of oxygen and inert gas in the final mixtures was the same as found in air.

The temperature in the ignition tube was measured every 10° up to the ignition temperature. First the spontaneous ignition temperature was determined (without the use of the spark). The flame was extinguished, the tube *b* was allowed to cool about 200°C or more and then was reheated. The spark was passed for 15 seconds every 10° during the process of reheating. If an ignition did not occur at the end of this time, the temperature was increased until it did. If an ignition occurred before 15 seconds the temperature was decreased. Thus an arbitrary time of 15 seconds of sparking was taken as the standard lag time. A sample of the gas mixture was taken for analysis.

The values of the ignition temperatures are given within the limits of regulation. The spontaneous ignition temperatures found ought not to be compared with ignition temperatures of methane-air mixtures recorded in the literature, since ignition temperatures vary with the method used.[6] Therefore, in this experimental work only relative ignition temperatures with and without the use of the spark discharge are of importance.

Results

The results show that the passage of the spark through one of the inert gases of the methane mixture causes a lowering of the ignition temperature, the extent of which varies with the gas passing through the spark. (Table I.)

If the flow of helium is doubled and the other gases kept constant (the approximate composition being 4.6 percent CH_4, 11 percent O_2, 84 percent He) no temperature lowering is observed at all.

All other conditions being the same in a given run, the amount of temperature lowering may be altered very materially by changes in the energy of the spark such as are obtained by altering the width of the spark gap.

[6] Bone and Townend, *Flame and Combustion in Gases*, 1927, p. 480.

Table I. *Showing the lowering of the ignition temperature of an 8 percent methane-"air" mixture when one of the constituents has been subjected to the passage of an electric spark.*

Gas passed through spark	Spontaneous ignition temperature, °C	Ignition temperature using spark °C	$-\Delta T$ °C
N_2	825–827	704–718	115
A	825–834	796–808	28
He	843–852	760–769	83
O_2 (commercial)	843–847	608–617	233
O_2 (electrolytic)	847–852	613–618	234
O_2 (from $KMnO_4$)	845–847	611–617	232

A series of runs was made varying the composition of methane from 2 to 20 percent and passing the spark through nitrogen. The results are given in Table II and plotted in Fig. 2.

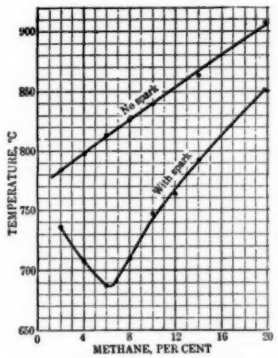

Fig. 2. Effect of composition of gas on ignition temperature.

The maximum lowering of the ignition temperature due to the spark occurs at about 6 percent methane. In the 2+ percent methane mixture, the flame was so pale in the apparatus that inflammation could not be observed easily in the usual way but had to be detected by sighting

Table II. *Showing the lowering of ignition temperature of methane-air mixtures when nitrogen is passed through the spark.*

Percent methane	Spontaneous ignition temperature, °C	Ignition temperature, (discharge passed through N_2), °C	$-\Delta T$ °C
2.+	779–790	734–749	43
4.3	793–797	704–713	87
5.9	811–814	685–690	125
7.9	825–827	704–718	115
10.05	838–843	746–749	93
12.18	855–	760–767	82
14.6	861–866	788–797	71
19.75	906–911	843–861	56

down the axis of the tube. The spontaneous ignition temperatures show a steady drop down to 2 percent methane.[7] However, when the spark is used, the ignition temperature reaches a minimum at about 6 percent methane. Presumably the two curves may meet (or nearly so) at some lower methane concentration, which point may not be without significance.

On placing three 80-mesh nichrome wire screens in the path of the gas mixture before it entered the ignition tube, the lowering of the ignition temperature due to the spark was found to decrease considerably. Also for equal ignition temperatures the sparking time or lag period was greater with the screens in position. This indicates that the metal screens removed something from the gas stream which had been introduced by the spark.

Somewhat but not widely different lowerings of the ignition temperature are observed when different materials (stainless steel, aluminum, carbon and nickel) are used as electrodes. This may be due to uncontrolled variations in the shapes of electrodes and to small variations in the width of the spark gap.[8]

If the spark is passed through the stagnant gas for 5 or 10 seconds and the flow of the gas sparked is delayed for some time (after cessation of spark) an ignition may still be observed at a reduced temperature when the flow is resumed. Delay times of 2 to 2½ minutes have been recorded. During this time several such post ignitions can be observed if the above sparked gas is preserved by stopping the flow immediately after each ignition takes place. The total delay time for a given period of sparking depends on the temperature in the tube *b* and the time the gas is allowed to flow after each ignition. With the screens in position this delay time was reduced to only 10 seconds. For practical reasons it was only possible to perform these experiments when the gas sparked was oxygen. It is evident that the species causing ignition possess a long life.

This effect is not observed at a reduced temperature if sparking is dispensed with and instead, ignition is brought about by touching the gas off with a flame at the end of tube *b*. If the flame at *d* is now extinguished, as before, by delaying the flow of oxygen, a second ignition does not occur when the flow is resumed.

On shortening the 1 cm tube to the left of *d* from 12 cm to its present length of 7.6 cm, a still further lowering of the ignition temperature due to the spark resulted.

Discussion

The passage of the spark through the aforementioned gases introduces some active carrier which, when carried into the methane stream, renders the latter more easily ignitible. A number of possible causes of the phenomenon will be mentioned and discussed.

Two properties of the carriers are conspicuous. They possess a relatively long life and are rather easily removed from the gas by metal screens.

A series of experiments was carried out to determine whether the lowering of the ignition temperature could have been due to the formation of NO[9] in the spark discharge. By means of a series of capillary tubes, different amounts of NO ranging from 0 to 0.15 percent were introduced[10] into an 8 percent methane-air mixture and the resulting lowering of the spontaneous ignition temperature due to the presence of NO was observed. A lowering of only 16°C was noted when as much as 0.013 percent of NO had been introduced. 0.15 percent of NO caused a temperature lowering of 250°C. This effect is of the same order as given by Coward and Wheeler.[11] In comparison

[7] The spontaneous ignition temperatures cited by Coward and Wheeler, Safety in Mines Research Board Paper No. 53, show a minimum at about 6 percent methane by using a static method in a heated quartz vessel. On the other hand, Coward and Guest, J. Am. Chem. Soc. **49**, 2479 (1927), also Guest (Technical Paper 475, U. S. Bureau of Mines), report the trend of spontaneous ignition temperatures similar to the present temperatures down to about 2.4 percent methane for gases in contact with heated metal bars. The difference is probably due to the methods used.

[8] See J. D. Morgan, Phil. Mag. **45**, 968 (1923).

[9] Ozone and nitrogen peroxide are known to enhance certain chemical reactions and to induce inflammation and explosion at temperatures lower than usual.

Semenoff and Rjabinin, Zeits. f. phys. Chem. **1B**, 192 (1928).

Spence and Taylor, J. Am. Chem. Soc. **52**, 2399 (1930).

Dixon and Gibson and Hinshelwood, Trans. Faraday Soc. **24**, 559 (1928).

[10] The NO rapidly oxidizes to NO_2 in the oxygen gas stream.

[11] Coward and Wheeler, Safety in Mines Research Board Paper No. 53.

with this, if one considers the oxygen gas used in these experiments which contained the largest percentage of nitrogen, that is, commercial oxygen (99.5 percent O_2; 0.5 percent N_2), the maximum amount of NO which could have been formed in the spark would have been about 0.004 percent NO in the final mixture of methane and air, yet nearly 250°C drop in ignition temperature is observed not only in this impure oxygen but also in pure oxygen when the spark is employed. Furthermore, a large effect is observed with rather pure nitrogen. It is concluded that the formation of NO cannot be responsible for the effect.

The formation of active nitrogen[12] and active oxygen[12] cannot be primarily responsible for the results since their decay at 500°C is much too rapid. The same is true of ozone[9] both as to rapidity of decay and the concentrations required to produce the effects observed. The above is especially evident in view of the post ignition phenomena and the fact that very appreciable effects are obtained with rather pure helium and argon.

Direct heating of the gas by the spark was negligible. Prolonged sparking caused a rise of only 5 to 10° at the mixing point which was no longer observable at the point where ignition occurred.

Catalytic action of dust from the electrodes was shown by numerous experiments not to be responsible for the phenomena. No incandescent particles could be observed in the dark. The effect was neither decreased nor augmented in an old and much used apparatus which had become coated with fine dust from electrodes. Moreover, the fact that with the same electrodes, widely different lowerings of the ignition temperature are observed when different gases are passed through the spark and when the methane content is varied, negatives the dust hypothesis.[13]

There remains as the most probable cause of the phenomena, the electrically charged gases or ions created by the spark. In favor of this are the relatively long life[14] of the active gas and its effective removal by metal screens. The ions are carried into the methane stream where they exert an action which facilitates combustion.

What the mechanism of the action is can only be conjectured, with the data available. The ions (positive and negative) may cluster molecules of methane and oxygen around them and form reaction centers.[15] Or an exchange of electrons may take place between the neutral methane molecule and the positive ion, thus ionizing the methane molecule and rendering the original ion neutral. The latter process is well known.[16] This type of collision will not occur unless the ionization potential of the primary ion is greater than that of the ion to be produced. The more nearly alike the two ionization potentials, the more probable the occurrence of the inelastic collision. Such electron transfers are further complicated by the masses of the two colliding systems and the amount of charge on the original ion.[17] If m is the mass of the impinging ion and M the mass of the atom to be ionized, the efficiency of ionization has a maximum for the condition $m=M$. For $m \gtrless M$ the efficiency falls off on both sides but much more rapidly for $m<M$ than for $m>M$. Furthermore, if mass and energy are kept constant the ionizing power of the impinging ion increases with decreasing charge.

The ionization potentials of the gases used are given in Table III. In a general way the data given in Table I—with the exception of the result for helium, which is rather surprising from this point of view—lend themselves to this concep-

[12] R. J. Strutt (Lord Rayleigh) Proc. Roy. Soc. (1911–16). E. J. B. Willey, J. Chem. Soc. (London) (1927–31). Bernard Lewis, J. Amer. Chem. Soc. **50**, 27 (1928); **51**, 654, 665 (1929).

[13] Since the completion of this work experiments have been published by Thompson (Zeits. f. phys. Chem. **18B**, 219 (1932)) on the effect of dust on the limits of explosion and the speed of flame propagation. Although these properties were not affected by dust in methane, an increase, if anything, in the ignition temperature, rather than a decrease, would be expected.

[14] Ions are known to possess long lives. J. J. Thomson and G. P. Thomson, *Conduction of Electricity through Gases*, 1928.

[15] S. C. Lind, *Chemical Effects of Radon*, A.C.S., Monograph 1927.

[16] Smyth, Harnwell, Hogness and Lunn, Nature **119**, 85 (1927). Hogness and Lunn, Phys. Rev. **28**, 849 (1926); **30**, 26 (1927). Harnwell, Phys. Rev. **29**, 683, 830 (1927). Smyth and Stueckelberg, Phys. Rev. **32**, 779 (1928).

[17] F. Zwicky, Proc. Nat. Acad. Sci. **18**, 314 (1932). R. M. Sutton, Phys. Rev. **33**, 364 (1929). R. M. Sutton and J. C. Mouzon, Physics **35**, 695 (1930). O. Beeck, Ann. d. Physik **6**, 1001 (1930). O. Beeck and J. C. Mouzon, Ann. d. Physik **11**, 737 (1931). O. Beeck, Proc. Nat. Acad. Sci. **18**, 311 (1932).

tion of the ionization of methane by collisions of the second kind.

TABLE III. *Ionization potential of gases.*[18]

Gas	Ionization potential
He	24.5
A	15.7
N_2	16.7–17
O_2	14.1–15.5
CH_4	14.5

The increased reactivity of ions over neutral molecules is recognized.[15] Such presumed methane ions may act as reaction centers by a clustering process, by direct enhanced reactivity toward oxygen or by the liberation of large amounts of energy during ion recombination, or by some other process. If clustering takes place around the original ion the apparent anomalous effect of helium can be understood on the basis of a greater field of force around ionized helium for which there is some evidence from the standpoint of chemical reactivity.[19]

The foregoing is presented only as a suggestion which should be capable of test. In particular, further work should reveal the relationships existing between the types of ions in the gas stream and the effects which they produce.

These experiments throw light on the process of ignition of a combustible gas mixture by the direct action of a spark passing through the mixture. They suggest that the ions formed in the path of the spark have a distinct auxiliary effect of their own, materially aiding the thermal energy liberated by the spark to bring about ignition of the mass of gas. This harmonizes the points of view of other investigators on this subject.[20]

[18] Int. Crit. Tab. H. D. Smyth, Rev. Mod. Phys. **3**, (3), 347–391 (1931).

[19] A. K. Brewer, private communication.

[20] Coward and Meiter, J. Amer. Chem. Soc. **49**, 396 (1927). Finch and Coward, Proc. Roy. Soc. **A116**, 529 (1927). Finch and Thompson, ibid, **A134**, 343 (1931).

Low Temperature Specific Heats: III. Molecular Rotation in Crystalline Primary Normal Amyl Ammonium Chloride*

J. C. SOUTHARD, R. T. MILNER AND S. B. HENDRICKS,† *Fertilizer and Fixed Nitrogen Division of the Bureau of Chemistry and Soils, and the Bureau of Standards*

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The heat capacity of primary normal amyl ammonium chloride was measured between 20° and 280°K. If the substance is quenched to 90°K a metastable form is obtained which upon heating above 165°K slowly changes toward an apparently stable form. Two regions of gradual transition were found. X-ray powder diffraction photographs taken above and below the transition regions were remarkably similar. The experimental results are interpreted on the basis of rotation of the $NH_3C_5H_{11}^+$ groups in the crystals.

L. PAULING[1] in his original work on the rotational motion of molecules in crystals considered the entropy of crystalline hydrogen and showed that the para molecules are rotating freely, even in the lowest state. He derived criteria for such motion and suggested that the gradual transitions shown by many solids accompany its excitation. The variations with temperature of some properties of crystalline sodium,[2] ammonium[3] and potassium nitrates[4] can be explained as arising from rotation of the nitrate groups.

Pauling suggested that the gradual transitions shown by HBr, HI, and the ammonium halides, and the transitions in solid N_2, O_2, and HCl accompany the excitation of molecular rotation. The abnormal increase in the dielectric constant of HCl[5] at its transition point and the accurate hexagonal close packed structure of solid nitrogen above 35.4°K[6] support such an explanation. It also is probable that the molecules are rotating in solid CO, C_2H_6, and CH_4 near their melting points. The high crystallographic symmetry of a number of ammoniates and hydrates at room temperature suggest that under such conditions the NH_3 and H_2O groups are spherically symmetrical.

In a number of other substances abnormal properties have been assumed to be caused by molecular rotation. Among these might be mentioned KCN,[7] $C_{21}H_{44}$, $C_{23}H_{48}$, $C_{24}H_{50}\cdots C_{31}H_{64}$, $C_{34}H_{70}$,[8] $C_{12}H_{25}OH$, $C_{18}H_{37}NH_3Cl$[9] SiO_2,[10] $Ca(NO_3)_2$, $Sr(NO_3)_2$, $Ba(NO_3)_2$, $Pb(NO_3)_2$,[11] and Na_2CO_3.

There apparently are but few cases in which the structural peculiarities of the crystals so determine the potential function as to permit rotation of groups with relatively large moments of inertia which would lead to detectable alteration of x-ray diffraction patterns. An illustration is afforded, however, by certain substituted ammonium salts. An exemplar is primary n-amyl ammonium chloride,[12] $NH_3C_5H_{11}Cl$, the x-ray dif-

* This is one of a series of five joint publications, the others of which will appear later in the Journal of the American Chemical Society. The calorimetric determinations were made in the Cryogenic Laboratory of the Bureau of Standards and the x-ray measurements in the Fertilizer and Fixed Nitrogen Division of the Bureau of Chemistry and Soils.

† We are indebted to Dr. F. G. Brickwedde for laboratory facilities; to Mr. J. W. Cook for the liquefaction of the hydrogen, to Mr. M. E. Jefferson and Mr. V. L. Mosley for assistance in the x-ray work, and to Mr. E. F. Jansen for purification of the amines used.

[1] L. Pauling, Phys. Rev. **36**, 430 (1930).

[2] F. C. Kracek, E. Posjnak and S. B. Hendricks, J. Am. Chem. Soc. **53**, 3339 (1931).

[3] S. B. Hendricks, E. Posjnak and F. C. Kracek, J. Am. Chem. Soc. **54**, 2766 (1932).

[4] T. Barth and F. C. Kracek, Phys. Rev. **40**, 1034 (1932).

[5] R. M. Cone, G. H. Denison and J. D. Kemp, J. Am. Chem. Soc. **53**, 1278 (1931).

[6] M. Ruhemann, Zeits. f. Physik **76**, 368 (1932).

[7] R. W. G. Wyckoff, *The Structure of Crystals*, New York, 1931, p. 364.

[8] A. Muller, Nature **129**, 436 (1932).

[9] J. D. Bernal, Nature **129**, 870 (1932).

[10] J. D. Bernal and W. A. Wooster, *Annual Reports of the Chemical Society, Crystallography*, London, 1931, p. 291.

[11] F. C. Kracek, S. B. Hendricks and E. Posjnak, Nature **128**, 410 (1931).

[12] S. B. Hendricks, Zeits. f. Krist. **74**, 29 (1930); Nature **126**, 167 (1930).

fraction characteristics of which have been thoroughly studied at room temperature and in which the rotating groups have sufficient scattering power to influence the intensities of x-ray reflection. The result of heat capacity determinations and x-ray diffraction photographs at various temperatures for this substance are described below.

Preparation of Material

The amine as purchased from the Eastman Company was first distilled from NaOH, and then from CaO. It was then twice fractionally distilled. The final material boiled between 104.6–105° (corrected, 747.4 mm).

The amine was dissolved in pure absolute diethyl ether and to it was added a solution of dry HCl in absolute ether. The precipitated salt was removed by filtration and washed repeatedly with dry ether. It was dried at 75° for several hours and then allowed to stand over $CaCl_2$ for some months before it was introduced into the calorimeter.

Heat Capacity Measurements

The heat capacity measurements were made with an adiabatic calorimeter described elsewhere.[13] The complex behavior of the compound entailed many unanticipated experiments.

If primary n-amyl ammonium chloride is cooled rapidly to below 165°K and then subjected to C_p measurements below that temperature, reproducible values are obtained. Such a quenched form when heated to about 175°K, spontaneously evolves heat at a sufficiently high rate to warm the calorimeter 0.1° per minute (maximum). Reproducible C_p measurements could not be made in the region between 165°K–230°K, but approximate measurements indicate no transition up to about 210°K. Between 210 and 230° the compound undergoes a gradual transition. The total amount of heat absorbed between 165 and 230°K is apparently a reproducible quantity since two measurements agreed to within 0.03 percent. From 230 to 242°K the heat capacity values were apparently quite normal and reproducible. Between 242 and 252°K a second gradual transition took place. Reproducible measurements of the energy of the transition, which was much smaller than that of the lower transition, could be made. The various energy values measured are listed in Table I, as are also the heats of transitions estimated by subtracting the graphically interpolated normal heats which presumably would have been observed had there been no transitions.

[13] J. C. Southard and F. G. Brickwedde. To be published.

Table I. *Heats of transition of n-amyl ammonium chloride.*

Quenched form	Run I cal./mole	Run II cal./mole
$H_{242.90}-H_{154.92}$ (measured; max. C_p at 221.5±0.5°K)	3944.1	3945.3
Estimated heat of transition	282.6	283.8
$H_{256.94}-H_{242.90}$ (measured; max. C_p at 246.5±0.5°K)	710.7	710.7
Estimated heat of transition	32.1	32.1
Annealed form		
$H_{229.21}-H_{199.37}$ (measured; max. C_p at 222.0±0.5°K)	1474.0 cal./mole	
Estimated heat of transition	215.4	
$H_{254.61}-H_{229.21}$ (measured; max. C_p at 246.5±1.0°K)	1811.8	
Estimated heat of transition	568.2	

If primary n-amyl ammonium chloride was allowed to stand at *ca.* 195°K for a number of days a second, apparently stable, modification was obtained. The results of a number of C_p measurements made on successive days are plotted as Fig. 1. A steady state upon which reproducible measurements could be made was slowly approached. This annealed form was used for C_p

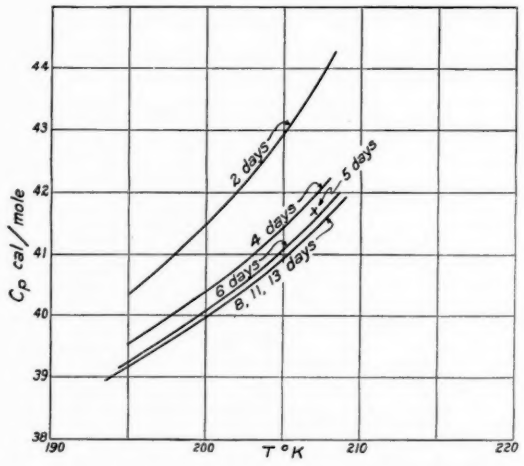

Fig. 1. The heat capacity of n-amyl ammonium chloride after annealing at 195°K for various times.

measurements from 14°K to above the ice point. It also showed two gradual transitions in the same regions as the quenched form; their magnitudes, however, were entirely different (Table I). Above 257°K the two forms had the same heat capacity.

Two attempts were made to regain the form upon which extensive measurements had been carried out by allowing the compound to stand at 195°K as before, in one instance for more than a month. The heat capacity curves obtained from these annealed forms were similar to that of the annealed form described above, but were not coincident with it. In one instance the values were somewhat low, in the other slightly high. In all these cases no change in C_p values with time were detected once a stable state had been reached.

In one experiment primary n-amyl ammonium chloride was cooled from room temperature to 230°K which is below the second transition but above the first. Heat capacity measurements were then made without evidence of the transition. The data indicate that there are at least three forms of primary n-amyl ammonium chloride. These are designated as A, B, and C, C being the form stable at room temperature. If it is assumed that the lower transition is characteristic of a change from a metastable form A to C, and the higher transition of some form, B to C, then it follows that all the measurements below 230°K were made on mixtures of A and B. The composition of the mixtures can be estimated from the heats of transition. On such a basis the quenched form contained 1.4 percent B, the annealed 25 percent B.

Heat capacity measurements on the quenched and annealed forms are listed in Table II and the transitions shown in Fig. 2. Since the heat capacity values of the two samples are the same above 257°K, it may be assumed that the compound has in each instance returned to the same form. If this form is taken as a standard state the differences in entropy between the two samples at low temperatures can be calculated from their heat capacities and transition energies. Such a calculation shows that at 20°K the difference in molal entropy between quenched and annealed forms is 0.15 E.U. This value possesses no significance since it is within experimental error. The

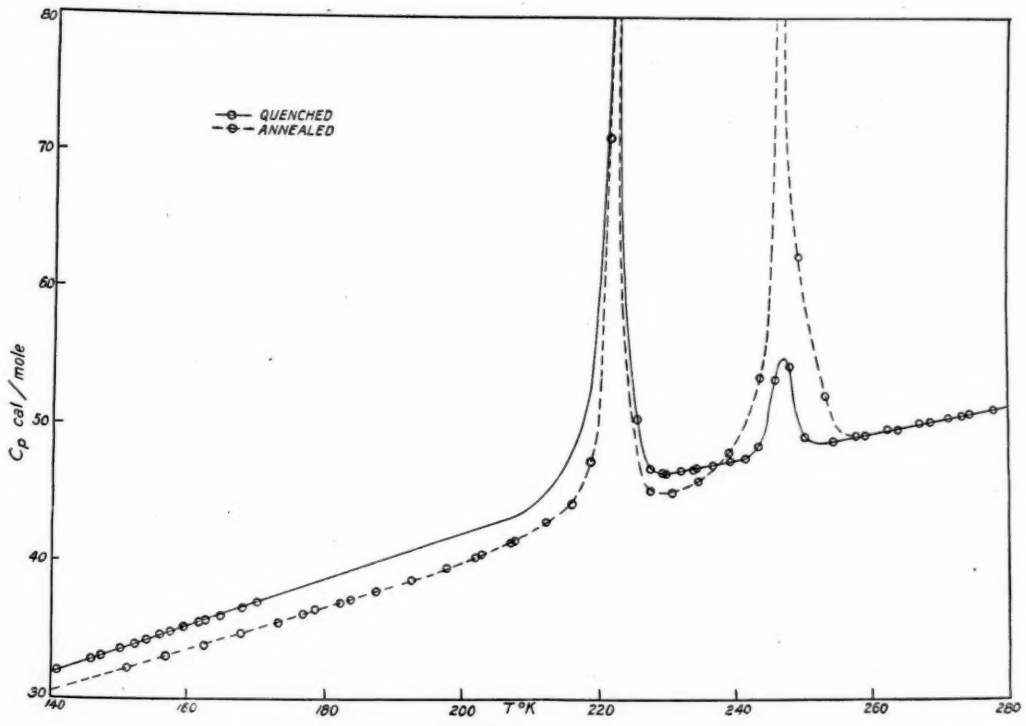

FIG. 2. Molal heat capacity of n-amyl ammonium chloride.

molal entropy of primary n-amyl ammonium chloride at 298.16°K is 63.74 E.U. as shown in Table III.

X-Ray Diffraction Characteristics

X-ray powder diffraction photographs of primary n-amyl ammonium chloride were made under various conditions suggested by the heat capacity work. It would have been far more desirable in the case of such a complex compound to make observations on single crystals but at low temperatures the technique for doing this would be somewhat involved and preliminary observations indicated that it would be difficult or impossible to prevent destruction of the crystals upon cooling. The perfect basal cleavage and micaceous character of the compound made it extremely difficult to obtain powder photographs free from effects due to crystal orientation.

The final type of diffraction camera used and the method of cooling the sample are shown in Fig. 3. In this apparatus the film is external to the vacuum system and can be changed without disturbing the sample. The sample, as shown by measurement does not differ in temperature from the cooling medium by as much as 5°. Its condi-

Table II. *Molal heat capacity of n-amyl ammonium chloride.*

Mol. wt. 123.58. Weight of sample (in vacuo) 29.646 g
273.16°K = 0°C

Quenched

T°K	C_p cal./mole deg.	T°K	C_p cal./mole deg.
July 2, 1931		July 22, 1931 (cont.)	
Liq. air bath		Liq. H_2 bath	
97.09	23.89	81.35	20.49
101.04	24.65	85.35	21.52
104.90	25.43	89.56	22.41
108.68	26.17	141.31	32.06
112.39	26.91	150.45	33.64
116.34	27.57	156.21	34.61
120.54	28.47	161.90	35.53
124.65	29.03	Nov. 17, 1931	
128.70	29.89	Liq. air bath	
132.69	30.48	147.66	33.14
July 8, 1931		152.51	33.95
Liq. air bath		157.62	34.81
125.94	29.29	162.82	35.64
129.98	30.08	168.02	36.49
133.95	30.79	225.65	50.39
137.88	31.42	227.70	46.80
146.37	32.85	229.83	46.44
150.70	33.65	232.09	46.65
154.98	34.36	234.47	46.86
159.23	35.06	236.86	47.04
July 20, 1931		239.37	47.39
Liq. air in vac.		241.71	47.53
66.20	17.46	243.58	48.49
70.80	18.11	245.85	53.33
75.09	19.01	248.02	54.30
79.20	19.98	250.26	49.11
83.51	21.08	252.60	49.14
88.03	22.13	254.96	48.93
92.38	22.95	257.34	49.08
96.62	23.80	259.72	49.25
100.75	24.59	262.09	49.45
104.77	25.41	Nov. 28, 1931	
113.53	27.27	Liq. air bath	
117.93	27.87	154.25	34.25
122.26	28.68	159.64	35.15
July 22, 1931		164.97	35.91
Liq. H_2 bath		170.23	36.92
22.34	4.36	CO_2 acetone bath	
26.21	5.53	229.48	46.53
30.60	7.00	234.00	46.79
35.44	8.50	238.51	47.20
40.64	10.05	254.58	48.79
46.64	11.70	259.31	49.16
52.68	13.41	264.04	49.58
58.20	14.96	268.76	50.14
63.37	16.25	273.48	50.61
68.24	17.39	278.19	51.00
72.84	18.42		
77.19	19.47		

Table II. (*Continued*).

Annealed

T°K	C_p cal./mole deg.	T°K	C_p cal./mole deg.
Nov. 2, 1931		Nov. 9, 1931 (cont.)	
Liq. air bath		Liq. H_2 bath	
176.98	36.04	39.64	9.59
182.28	36.85	45.26	11.30
187.53	37.71	50.80	12.69
192.73	38.55	55.85	14.21
197.87	39.46	60.59	15.35
202.95	40.52	65.09	16.39
Nov. 5, 1931		66.07	16.64
CO_2 acetone bath		70.27	17.54
202.50	40.42	74.48	18.53
207.77	41.54	78.71	19.42
Nov. 6, 1931		82.76	20.44
Liq. air bath		87.05	21.34
103.51	24.48	91.56	22.23
110.00	25.58	96.29	23.14
116.31	26.54	101.24	24.05
122.45	27.91	Nov. 11, 1931	
128.45	28.56	CO_2 acetone bath	
134.35	29.55	202.00	40.27
140.15	30.41	207.24	41.33
145.86	31.33	212.39	42.91
151.49	32.22	216.19	44.24
157.04	33.07	218.88	47.36
162.54	33.81	221.35	71.16
167.98	34.71	227.70	45.14
173.35	35.45	230.73	45.09
178.66	36.39	234.62	45.96
183.92	37.09	239.29	47.99
Nov. 9, 1931		243.72	53.44
Liq. H_2 bath		249.33	62.42
15.57	2.12	253.41	52.13
18.38	2.96	257.92	49.11
21.97	4.06	262.55	49.62
26.18	5.40	267.17	50.09
30.62	6.85	271.32	50.51
34.96	8.19	274.54	50.74

tion is readily observable at any moment. The camera radius was made about 10 cm in order to enhance the accuracy of the measurements.

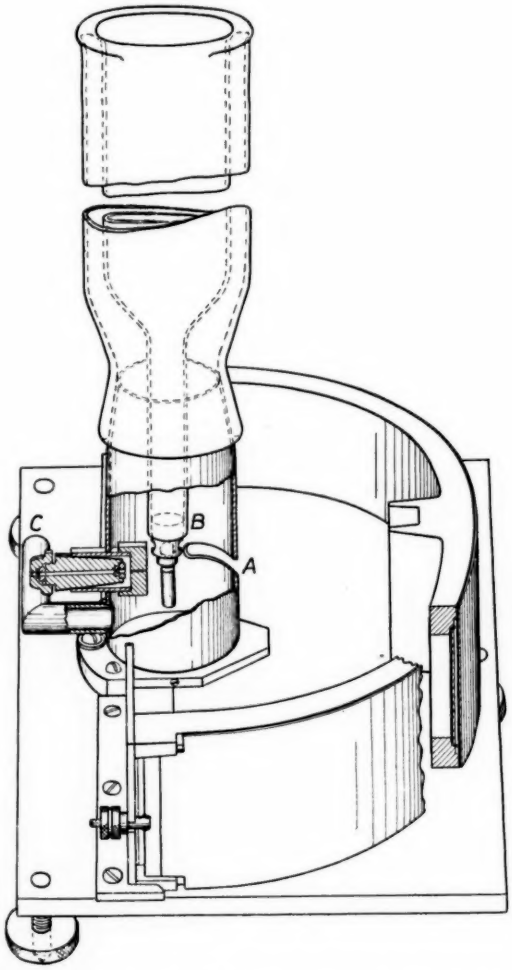

FIG. 3. X-ray powder diffraction camera for low temperatures with film external to the vacuum system; *A*, 5 mm slot covered with cellophane; *B*, copper to glass seal; *C*, tube leading to vacuum system.

Data from powder photographs of primary n-amyl ammonium chloride obtained under the following conditions are listed in Table IV. (1) Room temperature (298°K); (2) Liquid air temperatures (90°K); (3) Solid CO_2 temperature (195°K) after being heated from liquid air temperature; (4) Then allowed to stand for three days at solid CO_2 temperatures and photographed (195°K); (5) After the completion of (4) cooled to liquid air temperatures (90°K).

The same sample was used throughout this group of exposures. The lattice dimensions under these various conditions are:

(1)	$a=b=5.00$A,	$c=16.70$A,	$2C_5H_{11}NH_3Cl$ in unit
(2)	$a=b=6.81$,	$c=16.70$,	$4C_5H_{11}NH_3Cl$
(3)	$a=b=6.97$,	$c=16.70$,	$4C_5H_{11}NH_3Cl$
(4)	$a=b=7.06$,	$c=16.70$,	$4C_5H_{11}NH_3Cl$
(5)	$a=b=6.87$,	$c=16.70$,	$4C_5H_{11}NH_3Cl$.

It was assumed, as the standard for the measurements, that the lattice dimensions at 298°K are as listed above. These had previously been obtained from measurements on single crystals.

A number of untoward effects were evident on these photographs. It was practically impossible to obtain at 298°K a sample free from crystal orientation as shown by equality of intensities throughout the diffraction cones. This persisted upon cooling to 90°K and was accompanied by broadening of the diffraction maxima, which caused difficulty in detecting weak intensities. At 195°K, however, the orientation and the broadening were not observable. At the end of four days standing at 195°K the particle size had markedly increased. The only variable other than time was the slow accumulation of H_2O resulting from a minute leak in the system (the pressure was of the order of 10^{-5} mm of Hg).

TABLE III. *Entropy of n-amyl ammonium chloride*

0° to 20°K (extrapolated entropy)		1.28
20° to 298.16°K (measured entropy, disregarding transitions)		61.05
First transition 283.2/221.5		1.28
Second " 32.1/246.5		.13
	Total	63.74 E.U.

The change at 195°K upon standing is accompanied by an expansion of the lattice. In evaluating other changes a number of possible sources of error must be borne in mind. Possible impurities in the samples are H_2O, Hg, and CO_2. The Cu $K\alpha$-radiation contained some Cu $K\beta$ and Ni $K\alpha_1$, the latter from the base of a barium promoted Cu filament, the Cu being plated on Ni. At 195°K, before long standing, the presence, with moderate intensity of (210) was noted. This reflection could not be explained on the basis of a unit of

TABLE IV. *Powder photographic data from primary amyl ammonium chloride, Cu $K\alpha_1$ radiation (radius, 10.08 cm).*

Room temperature			Liquid air temperature. Sample cooled quickly			Solid CO_2 temperature. Sample warmed from liquid air temperature			After standing for three days at solid CO_2 temperatures			Liquid air temperature after standing for four days at solid CO_2 temperature		
$\sin^2\theta = 0.02359(h^2+k^2)+0.002126l^2$ $a=b=5.003(7.074)$ $c=16.70$			$\sin^2\theta = 0.01272(h^2+k^2)+0.00214l^2$ $a=b=6.813$ $c=16.70$			$\sin^2\theta = 0.01214(h^2+k^2)+0.00214l^2$ $a=b=6.974$ $c=16.70$			$\sin^2\theta = 0.01185(h^2+k^2)+0.00214l^2$ $a=b=7.064$ $c=16.70$			$\sin^2\theta = 0.01250(h^2+k^2)+0.00214l^2$ $a=b=6.874$ $c=16.70$		
Plane	$\sin^2\theta$ calc.	$\sin^2\theta$ obs.	Plane	$\sin^2\theta$ calc.	$\sin^2\theta$ obs.	Plane	$\sin^2\theta$ calc.	$\sin^2\theta$ obs.	Int.	Plane	$\sin^2\theta$ calc.	$\sin^2\theta$ obs.	Plane	$\sin^2\theta$ calc.	$\sin^2\theta$ obs.
(101)β	0.02100	0.02065	(111)β	0.02254	0.02226	(111)β	0.02160	0.02152	m	(111)β	0.02112	0.02117	(111)	0.02714	0.02647
(101)	.02572	.02557	(111)	.02759	.02726	(111)	.02642	.02647	v.s.	(111)	.02584	.02631	(111)Ni $K\alpha_1$	.03140	.03104
(102)	.03209	.03207	(112)	.03401	.03393	(111)Ni $K\alpha_1$	.03056	.03066	v.w.	(112)	.03226	.03229	(112)	.03356	.03320
(004)	.03402	.03403	(113)	.04471	.04477	(112)	.03284	.03280	m.s.	(200)β	.03872	.03884	(113)	.04426	.04322
(110)β	.03854	.03818	(200)	.05090	.05098	(004)	.03424	.03531	w	(113)	.04296	.04264	(200)	.05000	.05035
(111)β	.04027	.04020	(201)	.05304	.05317	(200)β	.03965	.03964	m	(200)	.04740	.04743	(201)	.05214	.05203
(103)	.04272	.04289	(220)	.10180	.10086	(201)β	.04142	.04088	m	(201)	.04954	.04959	(200)Ni $K\alpha_1$	.05786	.05837
(110)	.04718	.04687				(113)	.04354	.04277	m.w.	(203)	.06666	.06641	(201)Ni $K\alpha_1$	.06030	.06002
(111)	.04930	.04933				(200)	.04856	.04858	v.s.						
(114)	.08119	.08162				(201)	.05070	.05085	m.s.						
						(200)Ni $K\alpha_1$	.05640	.05702	m.w.						
						(201)	.05880								
						(210)	.06070	.06080	w						
						(203)	.06782	.06729	m.w.						
						(220)	.09712 }	.09910	m.s.						
						(221)	.09926 }								

structure containing $2NH_3C_5H_{11}Cl$. It is definitely absent at room temperatures as shown by photographs from single crystals previously reproduced. It is in a position that could not be confused with possible lines from any of the impurities mentioned above.

Intensity differences, previously reported, in diffraction patterns made under various conditions, are hardly trustworthy. Although there are apparently some true differences they are not considered of sufficient accuracy to emphasize.

DISCUSSION

The observation that the tetragonal unit of structure of primary n-amyl ammonium chloride at 298°K contains $2NH_3C_5H_{11}Cl$ requires the carbon and nitrogen atoms to be arranged collinearly in the $C_5H_{11}NH_3^+$ groups if they occupy fixed positions required by the crystal symmetry.[12] This arrangement is, however, different from that found in other long chain aliphatic compounds,[14] the x-ray diffraction data from which can be explained by a coplaner "zig-zag" configuration of the carbon atoms of a hydrocarbon group (Fig. 4). The observed intensities of reflections from (00*l*) of primary n-amyl ammonium chloride require the distances between scattering centers along the hydrocarbon chain to be 1.25A, which corresponds to the *projection* on the group axis of the arrangement shown in Fig. 4, d_3. This apparent difference in structure which for a time introduced considerable discord in the structure determinations of such compounds, is adequately explained by the concept of molecular rotation.

n-Amyl ammonium chloride has properties similar to both ionic and molecular compounds. A number of structural peculiarities are perhaps evident from an examination of the apparent unit of structure (base *ABCD*) and atomic arrangement shown in Fig. 5a. The value of a is but slightly greater than the corresponding value for the high temperature modification of ammonium chloride. (Compare Figs. 5a and b.) In fact the structure can be considered as made up of ionic layers simulating the "high" ammonium chloride arrangement separated by groups of two

[14] G. Shearer, Proc. Roy. Soc. (London) **A108**, 655 (1925); A. Muller, ibid. **A120**, 437 (1928).

molecular layers of long hydrocarbon groups parallel to the tetragonal axis; the two molecular layers being separated by a displacement along it in a manner such that they apparently do not interleave. This too is indicated by an increase of *ca.* 2.10A in the value of c_0 for each added methylene group in the homologous series. The area normal to the tetragonal axis occupied by a hydrocarbon group is 25.0A² which is markedly

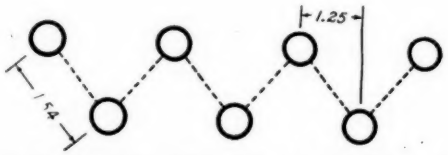

FIG. 4. Probable arrangement of carbon atoms in a saturated hydrocarbon molecule.

greater than the average value 18.0A² found for many fatty acids and strictly molecular organic compounds[15] but decidedly smaller than twice this value. This structural peculiarity apparently necessitated by the ionic nature of the compound might well be a factor in so determining the value of the potential function as to permit molecular rotation at room temperatures.

If crystals of primary n-amyl ammonium chloride are cooled to a sufficiently low temperature the rotation of the $C_5H_{11}NH_3^+$ groups must stop. In the equilibrium condition the various atoms would occupy positions required by the crystal symmetry. The diffraction pattern of such a material would, in the absence of polymorphic changes, be similar to that obtained at room temperature. There would, however, be some differences; notably, a change in the crystal symmetry and the appearance of reflections from planes requiring a larger unit of structure and possibly from (hko) with $(h+k)$ odd. The most striking characteristic of the diffraction patterns obtained from primary n-amyl ammonium chloride under various conditions is their close similarity. A reflection requiring a larger unit of structure is present on photographs at 195°K and probably on poorer photographs at 90°K.

The x-ray diffraction patterns afford no very conclusive answer to the question of the nature of the various unstable forms of primary n-amyl ammonium chloride encountered in the heat capacity measurements. An explanation consistent with the unusual behavior of this compound is suggested below.

In crystalline n-amyl ammonium chloride at 300°K the $NH_3C_5H_{11}^+$ groups are rotating about the tetragonal axis with an approach to constant angular velocity. If the compound is quickly cooled to some temperature below 165°K, the molecules are stopped in certain positions that are not the equilibrium ones. At such a temperature the rate of approach to the equilibrium state is very slow. However, if the compound is heated above 165°K some of the molecules have sufficient freedom to move into more stable positions with a corresponding evolution of energy. If the temperature is further raised to 195°K the rate of evolution of energy decreases markedly with time and finally it is possible to carry out adiabatic measurements of the heat capacity. The change to the stable configuration continues, however, and if a sufficient period of time has elapsed a heat capacity markedly lower than that of the quenched form is obtained.

The $C_5H_{11}NH_3^+$ groups apparently are not rotating in either the quenched or the partially annealed forms. If the temperature of either form is raised a region of gradual transition in which

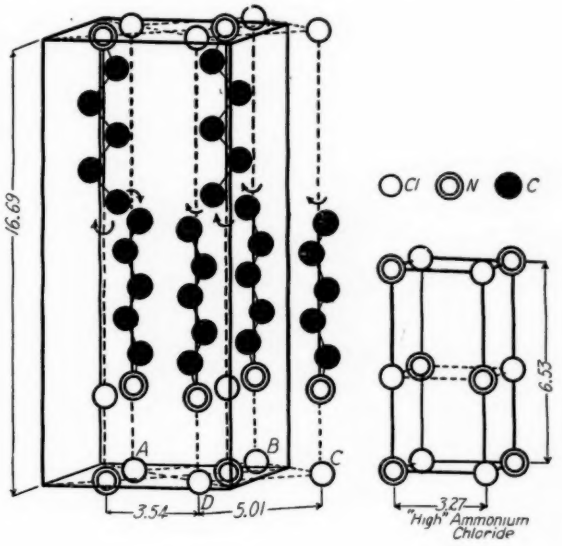

FIG. 5a. The atomic arrangement in n-amyl ammonium chloride.
FIG. 5b. A portion of the unit of structure of high ammonium chloride.

[15] A. Muller, Proc. Roy. Soc. (London) **A114**, 542 (1927).

molecular rotation sets in is reached. These temperatures are not the same for the two forms, indeed it is probable that that of the more stable form will be the higher. In practice, however, it is not possible to obtain what one might call the pure quenched or annealed forms. Thus it is expected that the various materials would show two transitions, the magnitudes of which would depend upon the time of annealing.

The presence of two transitions further suggests that the quenched and annealed forms partially exist in separate phases. If the quenched form is allowed to stand the molecules in a small crystal will slowly go into their equilibrium positions. When a sufficiently great number have changed the lattice as a whole becomes dynamically unstable and then quickly changes to the stable form. It is probable that few crystals of the stable form were present in the samples used for the x-ray diffraction photographs.

It might be pointed out that the case of n-amyl ammonium chloride is similar in principle to that of NO[16] (or N_2O_2) and CO.[17] In these cases it has been suggested that there is within the lattice a lack of discrimination in quenched forms between the stable positions of the molecules and ones differing from them by 180° rotation.

[16] H. L. Johnston and W. F. Giauque, J. Am. Chem. Soc. **51**, 3194 (1929).

[17] J. O. Clayton and W. F. Giauque, ibid. **54**, 2610 (1932).

The Heat of Expansion of a Gas of Varying Mass

L. J. GILLESPIE AND J. R. COE, Jr., *Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology* *

(Received November 2, 1932)

In this paper equations are given for the direct treatment of experiments in which not only heat, but also masses, pass the boundary of the container of the system during the experiment. The theoretical development is correlated with the treatment of Gibbs, and certain difficulties, mentioned by others, in the physical interpretation of his equations, are incidentally removed. It was found possible, within a reasonable time, to cause a gas to expand slowly enough from a calorimeter to simulate a reversible expansion, and the special equation developed for the heat of expansion with the aid of the Beattie-Bridgeman equation of state was verified by the results for the slow expansion of carbon dioxide and ammonia. In the case of carbon dioxide the effect of the deviations from the ideal gas law was to make the heat effect in excess of that calculated for an ideal gas by a sufficient amount so that the excess itself could be calculated within about 7 percent. A series of expansions of carbon dioxide was carried out at varying rates of flow, some as fast as permissible. The results, correlated by means of an empirical relation, serve to show that the results of the slow expansions correspond practically to an infinitely slow expansion. They also indicate that the heat effect for an infinitely rapid expansion is not zero for a real gas, but possibly vanishes with the pressure. In the absence of a perfectly sound method of calculating the heat effect for an infinitely fast expansion, a method is suggested which has at least the merit of agreement with the present experiments.

The bearing of the results on variable-pressure calorimetry, as practiced in experiments on the heat of adsorption, is briefly discussed.

I. INTRODUCTION

JOULE[1] measured the separate heat effects shown by a gas in expanding from one vessel into an originally empty vessel through a stopcock. He arranged his apparatus as shown in Fig. 1. R and E are two vessels connected by

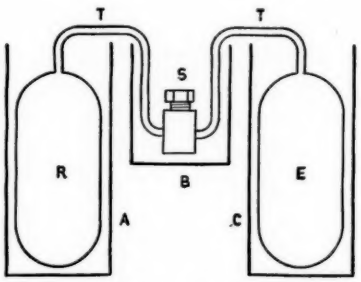

FIG. 1. Sketch of Joule's experiment.

small bore tubes T–T and a stopcock S. The vessels and the stopcock are immersed in water calorimeters A, B, and C. To quote from his paper, "One of the receivers (whose volume was 136.5 cu. in.) had 2828 cubic inches of dry air compressed into it, while the other (volume 134 cu. in.) was vacuous. After equilibrium was restored by opening the cocks, I found that 2.36° (Fahrenheit) of cold per pound of water had been produced in the receiver from which the air had expanded, while 2.38° of heat had been produced in the other receiver, and 0.31° of heat also in the can in which the connecting-piece was immersed."

We calculate by the use of the ideal gas law that 1.957 moles of air were initially present in the high-pressure vessel R, and 0.988 moles were left in it at the end of the experiment. The heat corresponding to 2.36° per pound of water is 595 g cal. The heat effect in the vessel R was therefore 614 g cal. per mole of gas escaping. For comparison, the value of RT may be taken as 574 cal. per mole at the temperature of the experiment, 288.7°C absolute.

Each of the vessels A, B, and C of Fig. 1 presents an example of a system open to exchange of mass with its surroundings. Such a system is called an *open system* by Defay,[2] in contrast to the *closed system*, across whose boundaries no mass is permitted to pass.

Problems involving the thermodynamics of open systems have been solved by special methods by chemists and physicists for special cases

* Contribution No. 294.

[1] J. P. Joule, Phil. Mag., series 3, May, 1845.

[2] Raymond Defay, Bull. Acad. Roy. de Belgique (Classe des Sciences) [5] **15**, 678 (1929).

in which the mass exchange takes place at constant pressure. Thus, when a gas enters or leaves a calorimeter at constant pressure and temperature the observed heat effect is taken equal to a change in the so-called heat content ($U+pV$, where U is the internal energy, p the pressure and V the volume). When a reaction takes place in a constant-volume calorimeter, the heat effect is equal to a change in the internal energy. When, however, the heat of adsorption of a vapor upon an adsorbent like charcoal is measured, we have to reckon with the fact that the equilibrium pressure of the system increases with the amount of vapor absorbed. The possibility that the heat effect is equal neither to the change of heat content nor to that of energy, but has a value lying between the two limits, was suggested by Williams.[3] Coolidge[4] showed, however, that "the observed heat will not differ from the true λ" when the gas is an ideal gas, provided that the temperature at which the gas enters the calorimeter is properly controlled, a condition which in practice would exclude a flow fast enough to make kinetic energy of importance, and which condition has in most cases not been imposed by the experimenter.

Gibbs used the idea of an open system solely for the purpose of defining the chemical potential. De Donder[5] and Defay[2] have written on the thermodynamics of open systems but have not interested themselves in the derivation of equations for the heat absorbed in actual experiments with open systems. The two laws of thermodynamics are announced for closed systems. Problems of opened systems can therefore be solved, if at all, by a comparison of the actual open system with an ideal closed system. The boundary of the open system is imagined shifted until it includes a constant amount of mass, and the ordinary thermodynamics of closed systems is applied, due account being taken of any significant difference between the original and the varied system. This is the method used in special applications.

It appears desirable, however, to summarize in equations the results of the shift of boundary, so that no shift of boundary is necessary in the application of the equations.

[3] Williams, Proc. Roy. Soc. (Edinburgh) **38**, 23 (1918).
[4] A. S. Coolidge, J. Am. Chem. Soc. **48**, 1795 (1926).
[5] Th. De Donder, Bull. Acad. Roy. de Belgique (Classe des Sciences) **15**, 615 and 900 (1929).

II. Equations for Open Systems

In order to retain a simple notation, sufficient for most cases, we shall suppose that when the volume of the system is varied, the external pressure against the boundary does not differ appreciably from the pressure of the system against it, and, similarly, when masses cross the boundary of the system at any point they have nearly the pressure at which they would be in hydrostatic equilibrium with the system at the given point. We shall also neglect the effects of gravity, electricity, distortion of the solid masses and capillary tensions.

The variation of energy, subject to the above general conditions, is

$$dU=dq-pdV, \tag{1}$$

where dq is the heat received by the system in a small change of state, p the pressure and dV the increase of the volume of the enclosure, when no mass crosses the boundary. If dm_1 units of mass of kind 1 are brought up to the system without adding heat or changing the volume V, the increase of energy of the system brought about by *shifting the boundary* to include the dm_1 units is u_1dm_1, where u_1 is the ordinary internal energy of the unit mass at its pressure p_1 (and volume v_1). Taking p_1 such as to allow smooth addition to the system, $p_1v_1dm_1$ is the increase of energy of the system of shifted boundary required to reduce the volume to the original volume V when no heat is transferred during the compression. Hence

$$(dU/dm_1)_{V,q}=u_1+p_1v_1, \tag{2}$$

where the subscript q indicates an adiabatic variation. The complete variation, for simultaneous transfers of heat and mass and variation of volume is

$$dU=dq-pdV+\Sigma(u_1+p_1v_1)dm_1, \tag{3}$$

where the summation is for all kinds of mass crossing the boundary and the dm's are taken algebraically.

If dq were a "perfect differential" like dU and dV, the substitution of partial derivatives in the expansion of dU in terms of the variations dq, dV and the dm's would call for no comment. Tunell[6] has emphasized that q is given by a line integral,

[6] George Tunell, J. Phys. Chem. **36**, 1744 (1932).

and that under certain circumstances dq is as true a differential of a function as any other. This is the case when a path for the line integral is fixed. In the present case we may suppose that all the heat is added or subtracted by means of a mechanism (used only for heat transfer) whose path of operation is arbitrarily fixed, thus making the heat added a function of a single variable. The relation $(dU/dq)_{V,m}=1$ is not affected by the nature or path of this mechanism and the choice of this path affects in no way the path which correlates the variations dq, dV, dm_1, etc., leaving these variations still arbitrary.

Eq. (3) is subject to the above stated restrictions relating to change of volume and exchange of masses with the surroundings, but applies to a system of any number of phases, either in internal equilibrium or not. This is because the energy of a system isolated by keeping dq, dV and the mass variations all zero cannot change. It applies to an enclosure in which a gas flame is burning. Gas enters, the products of combustion leave, and heat is lost from the surface of the enclosure by radiation and convection. If the volume is constant and we operate at a steady state, the variations of volume and energy with time are zero, and we have for the loss of heat

$$-dq=\Sigma(u_1+p_1v_1)dm_1 \tag{4}$$

or the loss of heat equals the heat content of the entering gas minus the heat content of the products of combustion. (dm being negative for these.) Note that we do not have to speak of the loss of heat with the products if they escape at a high temperature, as the loss of energy is fully included in the heat content term, $(u+pv)$.

In constant pressure calorimetry it is convenient however to make the exchange of mass occur at constant temperature, so that we can measure directly the increase of heat content ΔH attending a reaction at constant temperature. In this case

$$\Delta H=-\int dq. \tag{5}$$

ΔH is not always for the change of state in which we are most interested, and in writing the chemical equations we have to distinguish (except for mixtures of ideal gases) whether the products leave as a mixture, or separately as pure substances.

When some products leave at constant pressure, but other products remain as solids or liquids, or when the reactants are introduced into the enclosure at the beginning of the experiment, we do not have a steady state. Yet Eq. (5) holds in this case also. Suppose we measure the heat of vaporization of a liquid. Then the system is open to escape of vapor, but closed to entrance of liquid. The same heat would however be required to evaporate a given mass of liquid in the actual case as in an ideal case, in which water is slowly forced in as fast as it evaporates. For the ideal case differs only in that we should add the extra energy pv as work, where v is the volume of the added water, and should remove an equal extra quantity of energy, since the extra volume of vapor removed equals that of the water added. These considerations apply in the general case, provided only that the pressure is constant, including the case of a closed system whose pressure remains constant.

When no mass crosses the boundary, the variation of entropy is given by

$$dS=dq/T \tag{6}$$

subject to the general condition that the variation must be produced reversibly in all respects.

If dm_1 units of mass of kind 1 are brought up to the system without adding heat, then the increase of entropy of the system brought about by merely *shifting the boundary* so as to include also the mass dm_1 is s_1dm_1, where s_1 is the entropy of unit mass. If this mass has the temperature T of the system and such a pressure p_1 (and molal volume v_1) as would make it in equilibrium with the system through a wall permeable only to matter of kind 1, we can mix it reversibly and adiabatically with the system, for instance by merely pressing it into the system through a semipermeable membrane without adding or subtracting heat, and without any change of entropy of the system of shifted boundary. Therefore

$$(dS/dm_1)_q=s_1, \tag{7}$$

where s_1 is defined above. Hence the complete variation of the entropy, for simultaneous reversible transfers of heat and mass, is

$$dS=dq/T+\Sigma s_1dm_1. \tag{8}$$

Transfers of heat and mass together with adia-

batic changes of volume at constant mass are sufficient to produce every desired state of the system, and the change of entropy with volume at constant mass and adiabatically is zero.

If desired, the justification given above for ignoring the peculiarity of dq as a differential can be applied also to this case.

The consistency of Eqs. (3) and (8) with the Gibbs theory, in which dq does not appear, may be shown by eliminating dq from them. In this case we consider reversible variations only of a single phase. Thus all the quantities u_1, p_1, v_1, s_1 and T refer to the state of unit mass of kind 1 when it would be in equilibrium with the system through a membrane permeable only to this kind of mass, and similarly with regard to masses of other kinds. Elimination of dq from Eqs. (3) and (8) gives

$$dU = TdS - pdV + \Sigma(u_1 + p_1v_1 - Ts_1)dm_1, \quad (9)$$

where $u_1 + p_1v_1 - Ts_1$ is obviously the *zeta*-function of Gibbs per unit mass. This is shown by him to equal the chemical potential μ_1 in the case of a pure substance as above. Hence Eqs. (3) and (8) are consistent with his equation

$$dU = TdS - pdV + \Sigma\mu_1 dm_1 \quad (10)$$

and therefore with his entire system, since none of his equations contain dq.

Inspection of Eqs. (3) and (8) shows that the right-hand sides contain terms (u_1 or s_1) which depend on the standard states used to define zero or unit values of energy or entropy, whereas the left-hand sides contain only differentials of energy and entropy. These differentials also depend upon the choice of standard states in the present case, in which the total energy and entropy are regarded as dependent in part upon the total mass.

In the application of Eqs. (3) or (8) to cases where the state is not steady, it will be necessary to evaluate the left-hand members. For this it is obviously not necessary, but certainly convenient to observe that the energy of zero mass is zero, and the entropy of zero mass at a temperature other than zero is zero. In all cases in which the production of heat and work is at the expense of material changes, this is obviously permissible to assume in the cases of the energy and the free energy (of Helmholtz), and since the latter equals $U - TS$, the theorem for the entropy is established.[7]

One reason for here developing Eqs. (3) and (8) from fundamental thermodynamic principles rather than finding one of them from the other by comparison with Eq. (10) from Gibbs is that Gibbs' treatment has been held obscure by some authors. Thus, Milne[8] states: "Willard Gibbs simply introduced partial differential coefficients into a situation in which the ordinary 'physical' notion of a partial differential coefficient is physically not realizable. He considered the increase in energy of a system which occurs when its volume and entropy remain fixed but the mass of a chemical constituent is altered. How on earth (or in physics, which is the same thing) one can experimentally import matter into a system without importing or exporting entropy, or indeed knowing what entropy has been imported or exported, I have never been able to see, and the difficulty is largely responsible for the obscurity which is felt when reading Gibbs. The fact is that the idea is a purely mathematical one."

Also, Defay[2] states in part "W. Gibbs gave the principal equations which govern open systems. But his exposition is that of an intuition of genius which proceeds by leaps and which logic, advancing step by step, cannot follow. In order to build on a firmer foundation, De Donder, in his work *L'Affinité*, has voluntarily limited himself to the study of closed systems, a study which he has carried much further than Gibbs. With such systems, when one speaks of 'heat received by the system' or of 'work done by the system,' one knows exactly whereof one speaks.[9] It is not the same as respects open systems, as we shall see later."

Without maintaining that the treatment of Gibbs is in need of clarification, it may however be pointed out that Eq. (9) leads directly to

$$(dU/dm_1)_{S,V,m} = u_1 + p_1v_1 - Ts_1, \quad (11)$$

which suggests a direct physical interpretation of the chemical potential from its definition

$$\mu_1 = (dU/dm_1)_{S,V,m} \quad (12)$$

[7] These assumptions furnish a necessary justification for the omission of an integration constant in Gibbs' Eqs. (93) to (96).

[8] E. A. Milne, *The Aims of Mathematical Physics*, The Clarendon Press, Oxford, England (1929), quoted by Bancroft, J. Phys. Chem. **34**, 1614 (1930).

[9] "*de quoi il s'agit.*"

by the use of the sort of reasoning employed above in deriving Eqs. (3) and (8).

As a matter of fact Gibbs provides a physical interpretation, but postpones it to page 95 (of the reprinted paper) and, as usual, deals with entropy rather than heat.

III. Equations for the Heat of Expansion of a Gas of Varying Mass at Constant Temperature

We shall use Eq. (8) as a starting point, for convenience. Eq. (3) may also be used. In either case it is necessary to add a second-law equation (for closed systems). We shall consider only the case in which the gas does not change in composition during the expansion. Then the total entropy is given by

$$S=sm, \tag{13}$$

where s is the entropy of unit mass at the temperature and pressure of the gas, and m the number of units of mass.

Then we have in general

$$dS=sdm+mds. \tag{14}$$

Substituting in Eq. (8) we obtain

$$dq=Tmds. \tag{15}$$

The entropy of unit mass may be taken as a function of the temperature and pressure or of the temperature and the volume of unit mass. For the slow expansion at constant temperature we shall have for the integrated heat

$$\lambda=\int mT(ds/dp)_T dp=\int mT(ds/dv)_T dv, \tag{16}$$

which can be evaluated by the use of Maxwell's first and third relations as

$$\lambda=-\int mT(dv/dT)_p dp=\int mT(dp/dT)_v dv. \tag{17}$$

The last expression is convenient for the use of an equation of state implicit in the volume v of unit mass. This is equal to V/m, where V is the total constant volume of the container, so that

$$dv=-(V/m^2)dm. \tag{18}$$

Evaluation of the derivative dp/dT at constant molal volume by means of the Beattie-Bridgeman equation[10] gives a final expression for the heat

$$\lambda=RT(n_i-n_f)+\frac{RT}{V}\left(\frac{B_0}{2}+\frac{c}{T^3}\right)(n_i^2-n_f^2)+\frac{RTB_0}{V^2}\left(\frac{2c}{T^3}-b\right)(n_i^3-n_f^3)-\frac{RB_0bc}{2V^3T^2}(n_i^4-n_f^4), \tag{19}$$

where n_i and n_f are the numbers of moles of gas initially and finally present in the volume V. The gas constant R may be taken throughout as 1.987 cal.$_{15}$ per mole per degree centigrade absolute. The volume V is in liters, and the constants B_0 c and b are in liters per mole, as given by Beattie and Bridgeman for many gases. The absence of the constants A_0 and a is perhaps noteworthy.

For an ideal gas, all the equation of state constants except R are zero, and the heat absorbed is RT per mole. The result of Joule mentioned above is in excess over the value of RT by about 7 percent.

For a real gas, the heat effect is not solely dependent upon the number of moles escaping from the volume, but depends upon the numbers n_i and n_f separately, and this is true even of the first correction term.

Eq. (19) can be applied also to calculate the heat evolved at constant temperature when a gas is caused to flow slowly *into* a calorimeter.

By thus applying Eq. (19) to the vessels A and C of Fig. 1 and finding the change of energy of the sum of the systems A, B, and C, the heat effect of the middle vessel containing the stopcock can be determined by difference. The general result is not simple algebraically, but the effect is zero for an ideal gas.

IV. Apparatus

The apparatus used in measuring the heats of expansion is shown in Fig. 2, in which the relative dimensions of the various parts have been retained.

The expansion vessel is shown at D. It is made of one-thirty-second inch cold-drawn steel tubing with welded steel ends. Its volume, determined by filling with air-free water at 0°C and weighing, was 110.473 cubic centimeters in the experiments on carbon dioxide. Before the experiments on ammonia, a one-inch hole was drilled in the bottom and fitted with a threaded plug sealed by a

[10] J. A. Beattie and O. C. Bridgeman, Proc. Amer. Acad. Arts and Sci. **63**, 229 (1928).

copper washer. As a result of this change the volume of the bomb was 102.486 cubic centimeters for the runs on ammonia.

The bomb is connected by 0.0625 inch nickel-silver tubing to a steel cone and socket stopcock

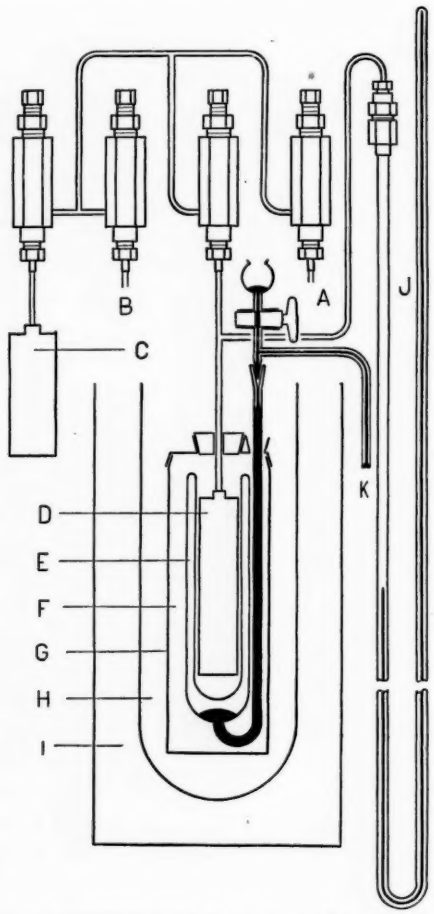

FIG. 2. Apparatus used in the present experiments.

through which it can be opened to the atmosphere at *A* by a second stopcock—to vacuum pumps at *B* by a third stopcock—or to the gas reservoir at *C* by a fourth. The manometer *J*, shown connected to the bomb by a tee-joint below the stopcock, was used only during the rapid expansions of carbon dioxide and was completely absent during the slow expansion of carbon dioxide and ammonia. This manometer is made of heavy-walled glass capillary tubing connected to the bomb by steel capillary tubing.

The heat effect is measured by an ice calorimeter *E* which encloses the bomb and 0.5 inches of the stem. The calorimeter is made of glass in the form of a Dewar tube filled with air-free water and mercury. When ice is frozen in the annular space *E* between the walls of the calorimeter, mercury is forced out of the capillary *K* into weighing bottles.

The calorimeter is enclosed in a water-tight, silver-plated copper can *G* to reduce heat exchange by radiation and is separated from it by an air space *F*. The metal can is in turn immersed in a freezing-mixture *H*. The freezing mixture used consists of an intimate mixture of finely-divided lead chloride and shaved ice. A relatively large proportion of lead chloride is used so that as the ice melts the liquid water will be practically immediately saturated with the salt. In this way a constant temperature a few tenths of a degree below zero is obtained which gives rise to a small and reasonably steady freezing of ice in the calorimeter.

The container of the freezing mixture is insulated by two inches of felt, *I*, and supported in a galvanized iron can. The calorimeter assembly is mounted on vertical rods (not shown) in such a way that it can be lowered away from the bomb to make way for a thermostat.

V. Preparation of Material

The carbon dioxide used was obtained in cylinders as a liquid and was dried by passing through phosphorus pentoxide. It was purified by three fractional sublimations, the first and last quarters being discarded each time. The solid was pumped down after each sublimation to remove any permanent gases. It was finally frozen into the storage vessel *C*, and the latter temporarily disconnected and weighed to determine approximately the amount present.

Liquid ammonia which had been dried by standing in cylinders over sodium was further purified by three fractional distillations, the first and last portions again being discarded in each distillation. Between distillations the ammonia was pumped to remove permanent gases.

VI. Experimental Procedure

The expansion bomb was first evacuated. It was then connected through the stopcocks to the reservoir which was kept immersed in an ice

bath. The bomb itself was immersed in a suitable thermostat so that the gas within it was at a known temperature and under the vapor pressure of the liquid at 0°C. When sufficient time had elapsed for equilibrium to be attained the stopcocks were closed. From these known values of the temperature and pressure the molal volume of the gas could be calculated by means of the Beattie-Bridgeman equation. By varying the temperature at which the bomb was thermostated, the molal volume of the gas in the bomb, and hence the amount of it, could be easily predetermined. The number of moles of gas loaded in was calculated from the molal volume and the volume of the container.

The bomb having been loaded, the thermostat was removed. The previously described freezing mixture was packed around the can containing the ice calorimeter, and after the latter had cooled to zero degrees, an ice mantle was frozen on its inner wall by means of a glass tube cooled in liquid air. The calorimeter was now raised into position around the bomb and the opening closed by means of a rubber stopper, more of the freezing mixture being added to cover the silvered can to a depth of two inches.

When sufficient time had elapsed for the system to reach a steady state, the creep of the calorimeter, that is, the slow freezing of ice due to heat being absorbed by the freezing mixture, was determined by weighing the amounts of mercury forced from K during three or four ten-minute intervals. The proper stopcocks were then opened and the gas allowed to escape very slowly into the atmosphere. When the expansion was completed the creep was again observed for three or four ten-minute intervals. The time required for the creep to return to a steady state was measured and the amount of mercury forced out in that time was corrected by subtracting the amount due to creep. The result was that amount due to the heat of expansion.

The magnitude of the creep was not the same for all experiments since it varied not only with the temperature gradient between the calorimeter and the freezing-mixture, but also with the atmospheric pressure and the room temperature. The effect of these last two variables was so small, however, that during any single experiment the mean deviation from the mean value of the creep was rarely more than 2 or 3 percent of the latter. The creep itself during the course of all the expansions ranged in value from 0.00220 to 0.00300 grams of mercury per minute.

The value for the ice calorimeter constant used was 0.01546 grams of mercury per 15° calorie—a value given by Ostwald[11] and redetermined by Lamb and Coolidge.[12]

VII. The Slow Expansions of Carbon Dioxide

The results of six slow expansions of carbon dioxide are given in Table I. In column 2 is given

Table I. *Expansion of carbon dioxide. Loaded at 20°C.*

1	2	3	4	5	6
Run No.	Atm. pressure mm	Δn	Calculated heat	Measured heat	Ratio Exp. heat: Calc. heat
1	752.5	0.1982	124.5	124.3±2.5	0.998±0.020
2	754.2	0.1982	124.5	121.4±6.9	0.975±0.055
3	753.0	0.1982	124.5	127.1±0.0	1.021±0.000
4	761.9	0.1981	124.5	123.6±0.3	0.993±0.002
5	749.1	0.1982	124.6	124.4±0.8	0.999±0.006
6	755.1	0.1982	124.5	124.8±0.6	1.002±0.005

the atmospheric pressure during each experiment. In column 3 is given the number of moles Δn of gas leaving the bomb. Preliminary experiments indicated that if the bomb be loaded at 20°C with the reservoir at 0°C, the gas in the expansion bomb will be sufficiently far from saturation when cooled to 0°C for the equation of state constants to be accurate. The values for the equation of state constants for carbon dioxide are:

$$A_0,\ 5.0065;\ a,\ 0.07132;\ b,\ 0.07235;$$
$$B_0,\ 0.10476;\ c,\ 66\times10^4;\ R,\ 0.08206.$$

The units are liters per mole, atmospheres, and °C absolute ($t+273.13$).

In calculating the molal volume, Bridgeman's[13] value for the vapor pressure of carbon dioxide at 0°C was used; 34.4009±0.0013 atm. at 0°C. The molal volume of carbon dioxide at 20°C and 34.4009 atm. is calculated from the Beattie-Bridgeman equation to be 0.54427 liters per mole. From this and the volume of the bomb it was

[11] Ostwald-Luther, *Hand und Hilfsbuch*, 3d Ed., p. 334.
[12] A. B. Lamb and A. S. Coolidge, J. Am. Chem. Soc. **42**, 1146 (1920).
[13] O. C. Bridgeman, J. Am. Chem. Soc. **49**, 1174 (1927).

TABLE II. *Expansions of ammonia at 0°C.*

1 Run No.	2 Atm. pressure (mm)	3 Temp. of loading (°C)	4 Δn	5 Calculated heat (15° cal.)	6 Measured heat (15° cal.)	7 Ratio Exp. heat: Calc. heat
1	756.1	217.86	0.006322	3.589	3.467±0.275	0.966±0.077
2	755.3	217.69	0.006331	3.594	3.415±0.130	0.950±0.036
3	763.6	218.28	0.006266	3.558	3.486±0.086	0.980±0.024
4	760.2	99.99	0.009870	5.660	5.679±0.152	1.003±0.027
5	757.6	99.92	0.009887	5.670	5.647±0.518	0.996±0.091

found that 0.20312 moles of carbon dioxide were loaded into the bomb before all runs. In calculating the amount of gas remaining after the expansion, the value 22.2612 liters per mole[14] for the molal volume at 0°C and one atmosphere was used and was corrected for deviations of the pressure from one atmosphere.

In column 4 is given the calculated value for the heat effect, obtained from Eq. (19). The measured value for the heat effect is given in column 5, and it will be observed that it is in substantial agreement with the calculated value. The possible deviation indicated is due to the slight deviation of the creep from the mean value. In column 6 is given the ratio of the measured to the calculated heat.

The time during which mercury was collected varied in these experiments from 55 to 85 minutes. That such a time is long enough to correspond to slow smooth flow of gas is indicated first by the above agreement, and second by a series of measurements at different rates of flow, reported below.

The value of $RT(n_i - n_f)$ was very nearly 107.5 cal. in all cases. The agreement of the measured excess heat over this figure with that calculated is to about 7 percent of the calculated excess.

VIII. THE SLOW EXPANSION OF AMMONIA

Many unsatisfactory experiments, not reported in detail, were made in which ammonia, loaded at 20°C, at 30°C, at 100°C, and finally at 218°C, was allowed to expand slowly. The results obtained at the three lower temperatures were in all cases higher than was expected from Eq. (19), the differences amounting to 75 percent at 20°; to 50 percent at 30°; and to 25 percent at 100°. The discrepancies at the two lower temperatures are attributed largely to inaccuracies in the equation of state constants at pressures so near the saturation value, while those observed at 100° are now believed to have been due to the presence of a water film on the walls of the expansion bomb.

Such a film would result in excessive adsorption of ammonia at the high initial pressure and this excess would be desorbed with an attendant heat absorption comparable to the heat of solution of ammonia in water, or perhaps higher, when the pressure falls during the expansion. A relatively small amount of adsorbed ammonia, therefore, would give a serious error in the observed heat effect. This hypothesis is borne out by the fact that when, before loading at 100°, the bomb was evacuated for four or five hours while being baked at 218°, the measured heat of expansion agreed with that calculated.

A small quantity of foreign material in the bomb might greatly change the absorptive properties. The bomb was opened, thoroughly cleaned, and the results shown in Table II were obtained.

In all these experiments the bomb was evacuated and baked at 218° before it was loaded. In column 2 is given the atmospheric pressure at the time of the expansion. In column 3 is given the temperature of loading. The thermostats employed were steam and naphthalene vapor baths; the true temperatures were obtained from vapor pressure data and the barometric pressure.

In column 4 is given the number of moles Δn of gas leaving the bomb during the expansion. In calculating the molal volume of the ammonia at the loading temperature the values for the equation of state constants used were:

A_0, 0.870175; a, 0.877102; B_0, 0.00766400;
b, 2.231074; c, 6.131196×10^6; R, 0.08206.

[14] J. A. Beattie and O. C. Bridgeman, J. Am. Chem. Soc. **50**, 3151 (1928).

The units are liters per mole, atmospheres, and °C absolute ($t+273.13$).[15] The Bureau of Standards value for the vapor pressure of ammonia at 0°C was used: 4.2380 atm.[16] The molal volume of ammonia was found from the Beattie-Bridgeman equation to be 7.08698 liters per mole at 100°C; and 9.44294 liters per mole at 217.96°C; these values were corrected in each experiment for the small deviations of the thermostats from these temperatures. The value of Beattie and Lawrence—22.0753 liters per mole at 0°C and 1 atm.—was used in calculating the number of moles of gas remaining in the bomb after the expansion. This number and the number initially introduced were calculated from the molal volumes and the volume of the bomb.

In column 5 is given the heat effect calculated from Eq. (19). In column 6 is given the measured heat effect with a possible uncertainty in calories due to the possible deviation of the creep from its mean value. The numerical values given to these uncertainties are probably excessive. The experimental values are in good accord with the calculated values as is shown in column 7 where the ratio of measured to calculated effect is given.

The time during which mercury was collected varied from 32 to 50 minutes.

The value of $RT(n_i-n_f)$ is about 3.4 cal. for the first three runs, and about 5.36 for the last two. The measured (and computed) heat is in such slight excess over this, that the excess is only verified by the experiments with an average deviation of 50 percent of the calculated excess.

IX. Rapid Expansions of Carbon Dioxide

In addition to the slow expansions of carbon dioxide and ammonia, a series of seven expansions at increasingly greater rates was made with carbon dioxide. The results of these experiments, numbered from 4 to 10, together with those of the last three slow expansions are given in Table III.

Table III. *Rapid expansions of carbon dioxide.*

1 Run No.	2 Barometric pressure (mm of Hg)	3 Δn	4 Calculated heat (15° cal.)	5 Measured heat (15° cal.)	6 Ratio 5/4	7 Time (minutes)
1	761.9	0.1981	124.5	123.6±0.3	0.9928±0.0025	57.633
2	749.1	0.1982	124.6	124.4±0.8	0.9986±0.0054	41.333
3	755.1	0.1982	124.5	124.8±0.6	1.0022±0.0051	32.583
4	765.3	0.1986	124.8	123.4±0.3	0.9885±0.0023	9.750
5	756.0	0.1986	124.9	119.7±0.2	0.9587±0.0014	2.583
6	759.9	0.1986	124.9	114.6±0.3	0.9175±0.0023	1.300
7	757.2	0.1986	124.9	110.1±0.2	0.8895±0.0018	0.767
8	769.3	0.1986	124.9	105.5±0.7	0.8446±0.0053	0.500
9	759.5	0.1986	124.9	91.9±0.3	0.7358±0.0025	0.267
10	763.3	0.1986	124.8	74.1±0.3	0.5936±0.0022	0.033

In column 2 is given the barometric pressure at the time of each experiment; in column 3 the number of moles Δn of gas leaving the bomb; in column 4 the heat effect calculated from Eq. (19) for slow expansions; in column 5 the measured heat effect; and in column 6 the ratio of the measured to the calculated heats. Since the bomb was loaded before the rapid expansions in the same way as before the slow ones, it is only necessary at this point to mention, in connection with the above, a correction which had to be applied in calculating the amount of gas in the bomb before the expansion. This correction arose from the fact that the manometer, described above, which was now attached to the bomb, remained at room temperature when the bomb was cooled to 0°. As a result some of the gas originally in it was transferred to the bomb, an amount so small, however, that it could be determined closely enough by use of the ideal gas law.

In column 7 is given the time required for the pressure to fall to 10 cm above atmospheric pressure. This time was measured by means of the manometer and a stop-watch, and it gives a good measure of the rate of expansion. The time required for the pressure to fall exactly to atmospheric pressure cannot be measured.

It will be observed that the fraction of the cal-

[15] J. A. Beattie and C. K. Lawrence, J. Am. Chem. Soc. **52**, 12 (1930).

[16] Bur. Standard Sci. Paper No. 369 (1920).

culated heat obtained decreases with increasing rate of expansion.

X. Discussion of Rapid Expansions

It was found empirically that by plotting the cube root of the time t required for the pressure to fall to 10 cm above atmospheric pressure against the natural logarithm of the fraction $1-X$ of the calculated heat which was dissipated a straight line was obtained. The intercept of the straight line and its slope were determined by the method of least squares with the following relation:

$$A-B(100t)^{1/3}-\ln(1-X)=0; \qquad (20)$$

where

$$A=-0.2389\pm0.0765$$

and

$$B=0.4376\pm0.0141.$$

The experimental values of X, the fraction of the calculated heat obtained, were smoothed by means of this line, and the actual values and the smoothed ones are given in Table IV.

Table IV. *Comparison of experimental values of X with values smoothed by the method of least squares.*

1 Run No.	2 Time	3 X Calculated	4 X Experimental	5 X_E-X_C
–	Infinite	1.0000	——	——
1	57.633	0.9997	0.9928±0.0025	−0.0069
2	41.333	0.9993	0.9986±0.0054	−0.0007
3	32.583	0.9988	1.0022±0.0051	0.0034
4	9.750	0.9897	0.9885±0.0023	−0.0012
5	2.583	0.9515	0.9587±0.0014	0.0072
6	1.300	0.9142	0.9175±0.0023	0.0033
7	0.767	0.8773	0.8895±0.0018	0.0122
8	0.500	0.8429	0.8446±0.0053	0.0017
9	0.267	0.7869	0.7358±0.0025	−0.0511
10	0.033	0.5904	0.5936±0.0022	0.0032
—	0.000	0.2125	——	——

From the value of the intercept A it appears that the heat effect does not become zero for an infinitely rapid expansion, but that the fraction of the calculated heat effect becomes from 0.2705 to 0.1499. According to this, the heat effect for carbon dioxide is from 33.77 to 18.72 calories when the gas is allowed to expand infinitely rapidly under the given experimental conditions in our apparatus.

This extrapolated value agrees with a value 31.6 cal. calculated for the following ideal state of affairs. In the unresisted infinitely rapid expansion the work is here supposed not paid for at the expense of the energy of the gas in the container, but the energy change of separating the molecules against van der Waals forces of the gas in the container is supposed to be at the expense of the gas remaining in the container at any time. This energy loss is made up by a flow of heat after the expansion sufficient to restore the initial temperature. Under these assumptions the energy loss can be computed to a first approximation from an integration at constant temperature[17] of the equation:

$$dU=n(du/dv)_T dv=n[T(dp/dT)_v-p]dv \qquad (21)$$

with respect to the variable number of moles in the container. The resulting equation, based on the Beattie-Bridgeman equation, is

$$\Delta U=\left(A_0+\frac{3Rc}{T^2}\right)\frac{\Delta(n^2)}{2V}+\left(\frac{3RcB_0}{T^2}-A_0a\right)\frac{\Delta(n^3)}{3V^2}-\frac{3RcB_0b}{T^2}\frac{\Delta(n^4)}{4V^3}, \qquad (22)$$

where $\Delta(n^2)$ indicates $n_i^2-n_f^2$, etc., and ΔU the decrease of energy.

We do not pretend to say how reasonable a representation of the actual conditions is given in this way, but it is the best way we can offer to explain the experimental value at an infinite rate of flow, and Eq. (22) is proposed in the absence of anything better. According to this equation the heat would drop to zero in the case of an ideal gas, or in the case of a real gas when the volume of the container is infinite.

XI. Application to Variable-Pressure Calorimetry

If charcoal is placed in the gas-free vessel C of Fig. 1 and a gas is admitted from vessel A, the heat evolved from vessel C at constant temperature is the measured heat of adsorption, and it remains to find the change of energy or of heat content for the adsorption process itself. In actual experiments the flow of gas has not always been throttled in a separate vessel B, nor even in any

[17] To a first approximation, because the value of the line integral depends on the unknown variation of temperature during the expansion for the Beattie-Bridgeman equation, though it does not for the van der Waals or Keyes equations.

definitely known position. The change of energy in C is partly due to the heat effect studied in this paper and represented by Eq. (19).

For an ideal gas, the heat of throttling (even at variable pressures) is zero, and the part of the heat effect due to influx of gas is RT per mole of entering gas, provided that the flow is very slow, a result agreeing with that of Coolidge.[4]

If, however, the flow is rapid the effect is less than RT per mole, as shown by our experiments, and the limiting value for infinitely fast flow is certainly close to zero, if not equal to zero. This is in agreement with the result of Williams,[3] as in practice the condition of Coolidge, that the temperature of the entering gas be controlled, is necessarily violated in rapid flow.

The correction for deviations from the laws of ideal gases depend on the location of the throttling valve and upon more apparatus constants than are usually reported by experimenters, and we do not therefore develop the application of Eq. (19) in this direction.

The Dispersion of Sound in Nitrogen Tetroxide and Its Interpretation in Terms of Dissociation Rate*

WILLIAM T. RICHARDS AND JAMES A. REID, *Princeton University*

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Several types of dispersion of sound which may be manifest in a dissociating gas are discussed. Of these only the heat-capacity dispersion and the dissociation dispersion need be considered under suitable experimental conditions. The expression derived by Einstein for the velocity of sound in a dissociating gas has been modified to include heat-capacity dispersion. The experimental procedure indicated by this for obtaining significant dissociation rate constants is outlined. Measurements on the velocity of sound in nitrogen tetroxide which have been made with apparatus of special design, are reported. The range of temperature studied is 0°C to 30°C, the range of pressure 132 mm to 670 mm, and the range of frequency 9 kc to 451 kc. The velocity of sound has been thus defined with an estimated error of ± 0.1 m·sec.$^{-1}$. The maximum dispersion which has been observed is about 5 m·sec.$^{-1}$. From these measurements it appears that the rate constant of the dissociation reaction is $4.8\times10^{4}\pm0.5\times10^{4}$ at 25°C and 260 mm. The activation energy obtained for the dissociation reaction is 13.9 ± 0.9 kg·cal. The rate constant appears to diminish slightly as the pressure is reduced. Since an upper limit for the heat capacity of nitrogen tetroxide is fixed by experiment, it is necessary to suppose that the effective molecular diameters for the activation process are at least three times those for ordinary kinetic collisions.

INTRODUCTION

MEASUREMENTS of the velocity of sound in nitrogen tetroxide date from the pioneer researches of the Natansons[1] who were concerned with the reaction $N_2O_4 \rightleftharpoons 2NO_2$ as an example of chemical equilibrium. More recently, following a suggestion of Nernst and Keutel[2] and its incorporation into a quantitative theory by Einstein[3] several attempts have been made to detect a variation in the phase velocity with frequency in the hope of obtaining information concerning the rate of the dissociation reaction. The most recent of these[4] reported that the dispersion of sound at 25°C, 250 mm and 80 kc was no greater than an experimental error of 0.5 percent. This was believed to set a lower limit for the dissociation rate which closely approached the maximum unimolecular rate to be expected from the kinetic theory of gases. The present communication describes an attempt to obtain more positive information by increasing the precision of the acoustical method for corrosive gases, and by using lower temperatures and higher frequencies than have hitherto been employed in this connection. Measurements have been obtained which show unquestionable dispersion and, if interpreted in terms of a reaction rate, give a reasonable and self-consistent kinetic picture. An objection may, however, be raised to this interpretation which was not foreseen in the treatment of Einstein. It has become apparent that some non-dissociating gases show dispersion of sound similar both in its magnitude and in its dependence on pressure, temperature and frequency[5] to that which is here considered due to a reaction rate. Since only these quantities may conveniently be varied in the study of the dispersion of sound no straightforward experimental distinction between dispersion due to heat capacity and that due to reaction rate appears possible at present. It is necessary, therefore, to examine

* An advance notice of this communication has been published in J. Am. Chem. Soc. **54**, 3014 (1932).

[1] Ed. and Lad. Natanson, Wiedemann Ann. d. Physik und Chemie **24**, 454 (1885).

[2] Keutel, Inaug. Diss. Berlin (1910).

[3] Einstein, Sitz. Ber. Akad. 380 (1920).

[4] Kistiakowsky and Richards, J. Am. Chem. Soc. **52**, 4661 (1930). A more complete historical survey is given in this paper.

[5] Herzfeld and Rice (Phys. Rev. [2], **31**, 691 (1928)) base an explanation of this dispersion, which was first observed by Pierce (Proc. Am. Acad. Sci. **60**, 269 (1925)) on a lag between translational and internal energy adjustment. Kneser has recently (Ann. d. Physik **11**, 761 (1931)) treated this from the standpoint of Einstein's dispersion theory, and has explored the case of carbon dioxide over a considerable frequency range. Measurements in this laboratory on carbon dioxide and carbon disulfide at various frequencies, temperatures, and pressures provide additional authority for this statement.

from a theoretical standpoint a system in which the heat capacity work and the dissociation work are covarient with frequency. For this purpose a brief review of the method used by Einstein becomes imperative. In order to conserve space this discussion will be given in qualitative terms as far as possible, and Einstein's equations, when rewritten, will be expressed in his notation.

The dispersion theory of Einstein

When a damped plane sound wave of phase velocity V and frequency ω is propagated in the direction x in a dissociating gas the pressure impulse may be written $\pi=\pi_0 e^{i[\omega(t-x/V)]+i\varphi-\beta}$ and the condensation impulse $\Delta=\Delta_0 e^{i[\omega(t-x/V)]-\beta}$ where the real parts of π and Δ represent pressure and density increments, t refers to time, and β is the damping coefficient. The substitution of these equations, after appropriate differentiation, into a wave equation of the usual form leads to the evaluation of the phase angle φ:

$$\frac{\omega^2}{V^2}-\beta^2=\frac{\Delta_0}{\pi_0}\omega^2\cos\varphi \qquad \frac{2\beta\omega}{V}=\frac{\Delta_0}{\pi_0}\omega^2\sin\varphi. \quad (1)$$

Considerations apart from these give for a gas in which sound is transmitted adiabatically

$$\frac{\pi}{\Delta}=\frac{P}{\rho}\left(1-\frac{\Delta(Pv)}{P\Delta v}\right) \quad (2)$$

when P is pressure, ρ density, v volume, and Δ in the final term refers now to a small change. The real part of (2) is equal to the squared phase velocity of sound modified by absorption.

By means of (1) and (2) it is possible to compute the angle φ for any gas with completely determined properties or, conversely, to determine a single unknown property of the gas from measurements of the velocity of sound. The case of interest here is a dissociating gas for which the equilibrium constant is K, the heat of dissociation D, and the heat capacity at equilibrium C_0. It is further postulated that the gas contains n_1 double and n_2 single molecules, the decomposition of the double molecules having a unimolecular rate constant k_1, and the association a bimolecular rate constant k_2. From chemical considerations it follows that

$$[C+C_\omega f(\omega)]\Delta T+P\Delta v-D\Delta n_1=0$$
$$R(n_1+n_2)\Delta T-RT\Delta n_1=\Delta(Pv) \quad (3)$$
$$\frac{KDn_1}{RT^2}\Delta T+\left(\frac{n_2}{v}\right)^2\Delta v+\left(K+\frac{4n_1}{v}+\frac{d}{k_2 dt}\right)\Delta n_1=0$$

where T refers to temperature. These equations differ from Einstein's only in the substitution of $C+C_\omega f(\omega)$ for the heat capacity C_0 which he considers constant. For the present purpose it will be sufficient to define $C_\omega f(\omega)$ as a part of the heat capacity which equals C_ω at very low frequencies and vanishes at very high frequencies. Since translational energy adjustments must be rapid in order that the gas may retain the elasticity necessary for the transmission of sound, the condition $C_0-C_\omega\geqq 3/2R$ is apparent. Each of the variable quantities in (3) is undergoing cyclic adiabatic changes of the type

$$\zeta=\zeta_0 e^{i\omega t} \quad (4)$$

where $\zeta=\Delta T$, Δn_1, Δv. The time derivative of (4) enters (3) for the quantities $C_\omega f(\omega)\Delta T$ and Δn_1, since it is postulated that these quantities depend on frequency. Differentiation of (4) gives directly the relation between Δn_1 and frequency. The dependence of $C_\omega f(\omega)$ on frequency must be inferred by postulating some mechanism by which this part of the heat capacity is excited. Kneser,[5] on the reasonable assumption that a double collision may degrade an excited molecule, or excite a molecule which is in a low energy state, arrives at a result which may be written

$$C_\omega f(\omega)=C_\omega/(1+i\omega\vartheta) \quad (5)$$

if ϑ is a time characteristic of the duration of vibrational energy in the molecule. The general form of (5) is independent of the assumptions used in its derivation, and it may, therefore, be employed with some confidence. If now (3) is solved for $-\Delta(Pv)/P\Delta v$ and the result substituted in (2) a complex is obtained which has the form

$$\frac{\pi}{\Delta}=\frac{P}{\rho}\left\{1+\frac{k_1[A_1-A_3\,\overline{C}_\omega(1+i\omega\vartheta)^{-1}]+i\omega R}{k_1[A_2+A_4\,\overline{C}_\omega(1+i\omega\vartheta)^{-1}]+i\omega[\overline{C}+\overline{C}_\omega(1+i\omega\vartheta)^{-1}]}\right\} \quad (6)$$

where $\overline{C}$ and $\overline{C}_\omega$ represent the parts of the average heat capacity of the mixed gases which are re-

spectively independent of and dependent on the frequency, and

$$A_1=\left(\frac{2D}{T}-\bar{C}\right)\frac{n_1}{n_1+n_2}+R\left(1+\frac{4n_1}{n_2}\right)$$

$$A_2=\frac{D^2}{RT^2}\frac{n_1}{n_1+n_2}+\bar{C}\left(1+\frac{4n_1}{n_2}\right)$$

$$A_3=\frac{n_1}{n_1+n_2}\qquad A_4=\left(1+\frac{4n_1}{n_2}\right). \tag{7}$$

Following the method of Einstein it will be supposed that the real part of (6) is equal to the squared phase velocity of sound modified only by absorption as indicated by (1). This gives the solution

$$V^2\frac{1-\beta^2V^2/\omega^2}{(1+\beta^2V^2/\omega^2)^2}=\frac{P}{\rho}\gamma \tag{8}$$

where γ, the ratio of adiabatic to isothermal compressibilities is given by,

$$\gamma=1+\frac{k_1^2[A_1A_2+\bar{C}_\omega(A_1A_4-A_2A_3)-\bar{C}_\omega^2A_3A_4]+\omega^2[R(\bar{C}+\bar{C}_\omega)+k_1\vartheta\bar{C}_\omega(\bar{C}A_3-RA_4+A_1)+k_1^2\vartheta^2A_1A_2]+\omega^4\vartheta^2R\bar{C}}{k_1^2(A_2+A_4\bar{C}_\omega)^2+\omega^2[(\bar{C}+\bar{C}_\omega)^2+2k_1\vartheta\bar{C}_\omega(A_2-A_4\bar{C})+k_1^2\vartheta^2A_2^2]+\omega^4\vartheta^2\bar{C}^2}.$$

When ϑ is very small (8) reduces to the case $C_0=\bar{C}+\bar{C}_\omega$ treated by Einstein; when ϑ is very large a corresponding reduction for the case $\bar{C}_0=\bar{C}$ is obtained. If in a nonassociated gas double collisions are considered molecular associations, k_1 becomes very large, and n_1 very small, and the expression given by Kneser emerges. Finally, when ϑ and n_1 are very small or, conversely, when ϑ and k_1 are very small, the well-known expression due to Laplace results.[6]

The effect of uncertainties concerning the heat capacity

The influence of heat capacity variations on the dispersion of sound in a dissociating gas may now be calculated. For this purpose it will be convenient to consider a gas at 280°K for which $P/\rho=3\times10^8$ cm^2 sec.$^{-2}$, $D=14$ kg·cal. per mole and $k=1\times10^4$ in rough analogy to nitrogen tetroxide. To make the case somewhat more unfavorable than may reasonably be expected in practice it will further be supposed that only 10 percent of the double molecules are dissociated at this temperature, and that half the molecular heat capacity at equilibrium may drop out of the adiabatic elasticity at high frequencies, leaving only 5 calories due to the translational and rotational freedom of rectilinear molecules. This makes $\bar{C}_0=10$ cal·deg.$^{-1}$ and $\bar{C}_\omega=5$ cal·deg.$^{-1}$ per mole at constant volume. The velocity of sound in this gas, calculated from (8) for the circular frequencies of 10^5 sec.$^{-1}$ and 5×10^5 sec.$^{-1}$ and various values of ϑ is illustrated in Fig. 1. The velocity of sound at these frequencies

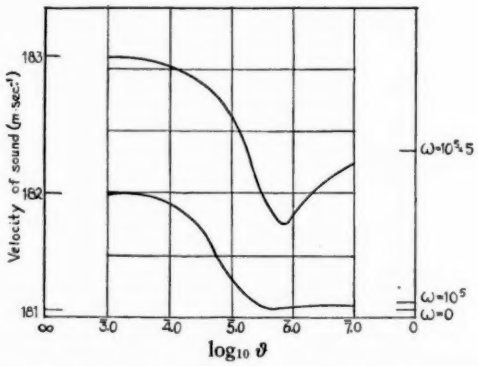

FIG. 1. Variation of the velocity of sound of various frequencies with the characteristic excitation time ϑ of the vibrational heat capacity in a dissociating gas having properties closely analogous to those of nitrogen tetroxide.

for a gas of the same properties except that $k_1=1\times10^8$ is given by Fig. 2. When the rate constant is small with respect to the frequency the situation need not here be considered.

If ϑ may be neglected in comparison with ω and k_1, and absorption is neglected, (8) may be rewritten in the more convenient approximate form

[6] The transition from (6) to (8) is unfortunately not as straightforward as it may at first sight appear. Indeed it is unwise to state unequivocally that (8) is the physically significant part of (6) until the development of (8) has been achieved with real quantities and an identical result obtained. This is difficult because when $C_\omega f(\omega)$ is introduced into (3) a harmonic of ω results which is not written in the original pressure and condensation waves. It is considered, however, that since (8) reduces to the forms given by Einstein, Kneser, and Laplace, all of which may readily be obtained with real quantities, the interpretation of (6) which is here adopted is justifiable.

$$k_1=\omega\left\{\frac{\overline{C}_0RT^2\alpha[2+\alpha(1-\alpha)]}{(2-\alpha)[\overline{C}_0RT^2+D^2\alpha(1-\alpha)]}\right\}\left\{\frac{V_\infty^2-V_\omega^2}{V_\omega^2-V_0^2}\right\}^{1/2} \tag{9}$$

when α is the degree of dissociation, and V_∞,[7] V_ω, and V_0 the phase velocities at high frequency, at the frequency ω, and at very low frequency respectively. For the case here under discussion V_∞^2, and V_0^2 are 36,000 and 32,780 $m^2\cdot sec.^{-2}$ from (8). When the assumption that ϑ is very small is not justified the value of k_1 calculated from (9) will not yield the true rate of dissociation. The magnitude of the error so introduced may easily be found by interpreting the dispersion sketched in Figs. 1 and 2 as wholly due to reaction rate.

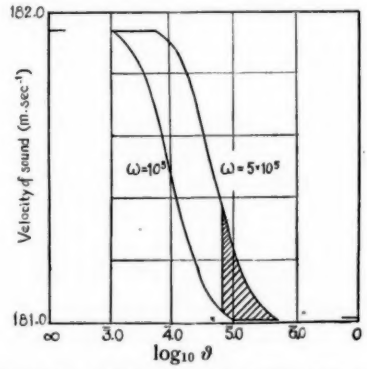

FIG. 2. Variation of the velocity of sound of various frequencies with the characteristic time ϑ in a dissociating gas having ten thousand times the dissociation rate constant of nitrogen tetroxide.

When k_1 is actually 1×10^4 $sec.^{-1}$ the rate constant calculated from (9) has a maximum value at $\vartheta=1.8\times10^{-6}$ sec. of 1.76×10^4 $sec.^{-1}$ for $\omega=1\times10^5$ $sec.^{-1}$ and of 1.34×10^4 $sec.^{-1}$ for $\omega=5\times10^5$ $sec.^{-1}$. Although not exact, these rate constants may be considered reasonably satisfactory. When k_1 is again actually 1×10^4 $sec.^{-1}$ and ϑ is actually not small, but very large, the rate constant calculated from (9) is more seriously in error; it is 2.28×10^3 $sec.^{-1}$ for 1×10^5 cycles and 7.47×10^3 $sec.^{-1}$ for 5×10^5 cycles. A discrepancy of this magnitude will be apparent from experiment, and may easily be corrected by an appropriate change of $\overline{C}_0$ in (9). If, therefore, the dispersion which is observed is partly due to change from the equilibrium heat capacity and partly to lag in the dissociation work, no grave difficulty in its interpretation need be anticipated.

When, however, the reaction rate constant is far greater than the frequency as pictured in Fig. 2, dispersion may be found in which the reaction rate plays no part, and its interpretation by means of (9) will then be wholly in error. In the region shaded in Fig. 2, which will be determined in extent by the magnitude of experimental error, an apparent rate constant will be found which is independent of frequency over a small range. This will change with temperature and pressure as ϑ changes, and hence may plausibly represent a dissociation reaction. Fortunately, the total increase of sound velocity which is to be anticipated from this cause is small in a gas for which the dissociation heat is greater than 10 kg·cal. In nitrogen tetroxide between 273° and 303°K, and from 150 to 600 mm pressure any velocity of sound which differs from that at any very low frequency by 1 $m\cdot sec.^{-1}$ or more may safely be attributed in part to lag in the dissociation work.

One further point should be made concerning the heat capacity which is not related to its possible variation with frequency. The heat capacities of the constituent molecules in a dissociating mixture cannot at present be obtained more than approximately either experimentally or from theoretical considerations. For this reason an uncertainty due to heat capacity is introduced into the calculated value of the dissociation rate constant even when ϑ is small and (9) is applicable. The influence of the heat capacity in (9) is strongly felt for two reasons, first, because it affects the compression work, and second, because it determines the value of V_∞. For reasons given above it is unlikely that experiment will yield a trustworthy value of V_∞, and this quantity must therefore be calculated by assuming a plausible $\overline{C}$. Thus uncertainty in k_1 due to heat capacity vanishes in a region of dispersion which is determined in extent by the experimental error, and which lies near the velocity at very low frequency. The accuracy of the rate constant obtained from (9) will, therefore, be in-

[7] The subscript ∞ means only that the frequency is much larger than k_1 and ϑ^{-1}. It may be shown by the kinetic theory that all gases become opaque to sound at very high finite frequencies.

creased if it is calculated from cases where $V_\omega - V_0$ is small, provided that it has been shown that ϑ may be neglected.

The experimental determination of the rate constant

If the argument given above is accepted, it is possible by suitable measurements to obtain values for the rate constant of the dissociation reaction which are free from error due to heat capacity uncertainties. Only the simplest case, in which the heat of dissociation is large, need here be considered.

No measurement of the dispersion of sound at a single frequency is sufficient to determine the rate constant. If the principles set down above are strictly applied it is necessary to employ two frequencies at each temperature and pressure, and it is further necessary that the higher of these frequencies should in each case show a dispersion significantly greater than the maximum which can be produced by heat capacity change. If, under these conditions, the rate constants given by both frequencies are the same, the effect on the rate constant of uncertainty concerning the equilibrium heat capacity may be eliminated by interpreting very small dispersions, measured with lower frequencies, as due wholly to change in dissociation work with frequency. The enormous labor involved in this procedure may greatly be reduced in the case of nitrogen tetroxide between 0°C and 30°C by a single assumption concerning the temperature coefficient of the mean lifetime of the excited molecule. This quantity may vary greatly with temperature only if a relatively small proportion of the total number of double collisions results in molecular excitation. Whatever the nature of $\overline{C}_\omega$ it is hardly conceivable that the "activation energy" required for its excitation should be very much greater in order of magnitude than that of the chemical reaction if, at a particular temperature, $\overline{C}_\omega$ is to participate in the adiabatic cycle. Hence it is permissible to assume that the temperature coefficient of ϑ^{-1} is equal to or less than that of k_1. When this is the case any change in $\overline{C}_\omega f(\omega)$ from the value $\overline{C}_\omega$ will be most apparent at the highest of the temperatures at which observations are made. If concordant values of k_1 are obtained from (9) at this temperature with two widely separated frequencies it may be concluded that $\overline{C}_\omega f(\omega) = \overline{C}_\omega$. In a small range of temperature below this the same conclusion will be justified if ϑ^{-1} conforms to the assumption made above that its temperature coefficient is not inordinately large. A procedure of this kind may be applied only, however, when the dissociation work in the sound wave is far greater than that due to $\overline{C}_\omega f(\omega)\Delta T$; it must be regarded with suspicion when applied to dissociating gases for which the heat of dissociation is small, or in which the degree of dissociation is near to unity. An additional sense of security will independently be gained if, at the lowest of the temperatures which are to be considered, a dispersion is obtained which far exceeds that possible from the change $\overline{C}_\omega f(\omega) = \overline{C}_\omega$ to $\overline{C}_\omega f(\omega) = 0$.

In the following sections very small dispersions, which have been shown to represent reaction rates by this argument, will so be interpreted without further discussion.

Experimental Method[8]

In view of the convenience with which magnetostriction oscillators of various frequencies may be prepared, they were used throughout this investigation. The electrical circuit for driving them has been described by Pierce[9] and the analysis of the frequencies so produced has been treated, following Pierce, in the previous communication from this laboratory. No change in this aspect of the magnetostriction method was found necessary.

The tube-dispersion

It has long been known that dispersion of sound appears when its velocity of propagation is measured in small cylindrical tubes. Since it is of secondary interest in this communication, it will be treated as an experimental tube-correction. A brief discussion of its nature, magnitude, and dependence on frequency will be given at this point in order to separate it from the wholly different and unpredictable dissociation-dispersion.

[8] In this and the succeeding sections the abbreviation kc will denote kilocycles sec.$^{-1}$, and will refer always to linear frequencies.

[9] Pierce, Proc. Am. Acad. Sci. **63**, 1 (1928).

Helmholtz and Kirchhoff[10] have developed an expression which describes with fair success the dispersion of sound in cylindrical tube. This may be written

$$V_\omega = V_0\left(1-\frac{(\gamma\eta)^{1/2}+(\kappa/C_v)^{1/2}(\gamma-1)}{2r(\gamma\omega\rho/2)^{1/2}}\right) \quad (10)$$

in which the quantities not previously defined are η, the viscosity, r, the radius of the tube, and κ, the thermal conductivity. According to this the velocity of sound in a particular gas in a tube of finite radius at a finite frequency should always be less than that at zero frequency in free space, and the difference between the two should increase as the wave-length increases or the radius diminishes. With a dissociating gas this difference increases sharply in the region of dissociation-dispersion[11] for, although the decrease in apparent C_v to be expected from Einstein's theory is almost exactly balanced by a corresponding decrease in κ, $\gamma-1$ may change from 0.08 to 0.25. Adequate values for η, κ, and C_v are lacking for nitrogen tetroxide, and the exact extent of the change to be expected under a given set of experimental conditions is, therefore, not accessible, but an exceedingly rough calculation shows that the tube-correction will approximately double when the dissociation work has been eliminated at very high frequency. Since, however, this change is only of the order of 5 percent of the dissociation-dispersion under the experimental conditions outlined below, the small correction which should be added to the observed dissociation-dispersion has here been neglected. The reaction rate constants calculated from (9) are then somewhat too large, but the error so introduced is believed to be considerably inferior to that due to other causes.

The dispersion produced in free space by the viscosity and heat-conduction of the gas should also be taken into account in any comprehensive theoretical treatment. This alters the phase velocity in the opposite sense to the tube-correction. Under the experimental conditions described below, however, its influence is far inferior to that of the tube walls, and may be wholly neglected with safety.

Apart from uncertainty concerning the damping constants of nitrogen tetroxide it appears unwise to apply (10) literally for the evaluation of the tube-correction under the experimental conditions herein employed. The measurements reveal, in common with all piezoelectric or magnetostrictive determinations, slight variations in the average half-wave-length with the distance from oscillator to reflector. These may be attributed, at least in part, to path differences between the main compressional impulse emitted by the oscillator and its subsidiary parts, with consequent interference and slight displacement of the points of maximum reaction measured in the acoustical chamber. Thus the assumption of a pure phase sinusoidal wave from which (10) was developed is violated, and simultaneously a number of variables are introduced about which little exact information is available, such as the reflection coefficients, amplitudes, and mass reactions of the various parts of the wave. For this reason it was considered expedient to calibrate the tube and oscillator with various nondissociating gases, and to apply the tube-correction indicated by these to the measurements on nitrogen tetroxide. Great confidence may be placed in the tube corrections so found, for they accord with (10) not only in sign, but also in magnitude as nearly as an estimate may be formed from the somewhat uncertain properties of the various gases. The tube-corrections indicated below are not, however, to be considered as tests of the Helmholtz-Kirchhoff theory, for they contain also corrections for the standard procedure used in measuring and averaging the various sound velocities.

A new and startling type of tube-dispersion, which has recently been discovered by Boyle and his co-workers[12] in liquids, is due to the absorption of longitudinal vibration and its transference into radical vibration at resonant frequencies of

[10] Helmholtz, Gesam. Wiss. Abh. Leipzig **I**, 383 (1882). Kirchhoff, Pogg. Ann. **134**, 177 (1868). More recent information on this subject may be found in Cornish and Eastman, Phys. Rev. [2], **33**, 90 (1929); Henry, Proc. Phys. Soc. **43**, 341 (1931).

[11] This statement is made on the assumption that (10) may be applied literally at any frequency to any gas whatever. A theoretical investigation of this assumption would be of interest, but could scarcely lead to corrections of magnitude which need here be considered.

[12] Boyle, Froman and Field, Canadian J. Research **6**, 102 (1932). Field and Boyle, ibid. **6**, 192 (1932).

the latter. While this is not specifically excluded for gases by the theory of Field,[13] it has been proved absent in the present work by the calibration of the tubes with gases of almost identical acoustical properties to those of nitrogen tetroxide, and by obtaining velocities of sound at the same frequency in two vessels of different diameter which differ only by the Helmholtz-Kirchhoff correction.

Apparatus for measuring the velocity of sound as a function of temperature

The problem of measuring velocities of sound at temperatures far from that of the room centers about the design of a suitable acoustical chamber. It is necessary that this be wholly immersed in the thermostating fluid to prevent temperature gradients. The oscillators must be supported rigidly to prevent change of position, and yet delicately to insure a large amplitude of oscillation. All materials of which the chamber is constructed must be highly resistant to the corrosive action of nitrogen tetroxide. Finally, the position of the movable reflector must be measurable with a high degree of precision. These conditions are satisfied by the acoustical chamber illustrated in Fig. 3.

The high- and low-frequency oscillators are marked *A* and *B* respectively. The ends of both measured 2.4 cm. The high-frequency oscillator operated at about 92 kc and was made of nichrome steel. It was supported on its dynamical center in alignment with the axis of the tube by means of a stout tungsten rod, *C*, sealed into the glass of the chamber itself. The low-frequency oscillator was a nickel tube of 2.2 cm outside, and 1.6 cm inside diameter. At each end of this solid nickel disks were fastened with gold solder; these served for the actual transmission of the sound impulse to the gas. This structure, being too heavy for support on a tungsten rod, was held free from constraint and in alignment by a sleeve of glass tubing fitted closely both to the interior of the acoustical chamber and to the exterior of the nickel tube.

The reflecting piston *D* was made entirely of glass, and enclosed a small bar of soft iron. Since the faces of the reflector must be normal to the axis of the acoustical chamber, they were ground on a glass lathe of special design. The position of the reflector was changed by means of a laminated-core magnet diagrammatically represented as *E* in Fig. 3, and changes were measured with a cathetometer to 0.005 cm. The magnetic field was

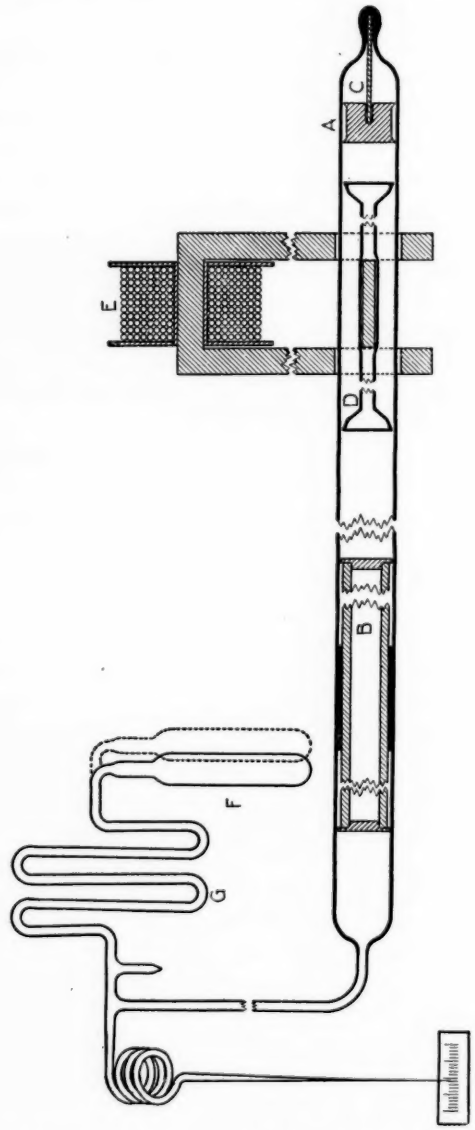

FIG. 3. Apparatus for measuring the velocity of sound in a corrosive dissociating gas as a function of temperature.

first adjusted to "float" the reflector in the acoustical chamber, and the magnet was then moved on a runway by means of a small-pitch driving screw. This secured great precision of movement, eliminated the packed joint neces-

[13] Field, Canadian J. Research **5**, 131 (1931).

sary with a thread drive, and made possible the use of two oscillators in the same tube. The response of the reflector to small impressed forces was so sensitive that it often migrated automatically to points of minimum motion in the standing-wave pattern. If its motion was not sufficiently smooth the faint vibration given by a small electric buzzer mounted on a remote part of the apparatus was sometimes helpful.

The Pyrex tubing of which the acoustical chamber was constructed had an internal diameter of 2.5 cm and was especially selected from a large stock for uniformity of bore and smoothness of internal wall.

The thermostat employed was filled with kerosene and provided with powerful stirrers. The temperature was regulated by hand to the precision necessary to define the velocity of sound. Irregularities of temperature at once manifested themselves by irregularities in the wave-pattern at points distant from the face of the oscillator. In general, the required accuracy was 0.05°C. Low temperatures were secured by circulating kerosene from the bath through a copper coil immersed in calcium chloride solution at −25°C. Condensation of moisture from the air, with consequent power loss in the oscillators, necessitated frequent changes of the bath liquid.

Pressure regulation in the acoustical chamber was secured by a small bulb F which was immersed in a large water-filled Dewar flask at an appropriate temperature. The bulb was kept in mechanical agitation to secure pressure equilibrium at all times. The glass spring G prevented the transmission of this impulse to the acoustical chamber. The pressure was read with a quartz spiral manometer.

The nitrogen tetroxide employed was made by heating lead nitrate in a stream of oxygen. It was then distilled with oxygen through phosphorous pentoxide, and finally distilled in vacuum before being distilled into the apparatus. These precautions, while in general adequate for the exclusion of the lower oxides of nitrogen and the permanent gases, were not sufficient wholly to eliminate small quantities of nitric acid.

The tube-correction for this apparatus was small and easily defined by the measurements with nondissociating gases summarized in Table I. Each value given is the average of at least three independent determinations of the velocity of sound with the same filling of gas. Since the difference between the velocity at 9 kc and at 92 kc was alone the quantity of importance, no attempt was made to eliminate small traces of impurities from the gases. The absolute velocities hence may be slightly in error. The tube-correction for this apparatus for nitrogen tetroxide is evidently $+0.4$ m·sec.$^{-1}$ at 9 kc. At 92 kc it may, therefore, be neglected according to the equation of Helmholtz and Kirchhoff. The velocity of sound in 99.98 percent argon at 92 kc was found to be 324.0 meters·sec.$^{-1}$ at 30°C and 760 mm pressure. This accords well with the velocity 324.2 meters·sec.$^{-1}$ calculated for these conditions from data found in the *International Critical Tables*, and substantiates the conclusion that the tube-correction may be neglected with this oscillator.

TABLE I. *Determination of the tube-correction for 9 and 92 kc 2.4 cm oscillators in a 2.5 cm glass acoustical chamber.*

Gas	P mm	T°C	V_9 m·sec.$^{-1}$	V_{92} m·sec.$^{-1}$	Tube-correction $V_{92}-V_9$
Pentane	342	30.2	190.16	190.62	+0.46
	343	30.2	190.25	190.62	0.37
	342	30.2	190.26	190.65	0.39
Air	760	30.0	349.42	350.02	0.60
	760	18.9	342.60	343.13	0.53
	140	30.0	349.40	350.04	0.64

Apparatus for measuring the velocity of sound at frequencies above 90 kc

At frequencies much above 92 kc the use of oscillators of 2.45 cm cross section becomes impractical owing both to mechanical difficulties of support and alignment, and to the inaccuracy of the cathetometer in estimating half-wave-lengths corresponding to very small displacements. An acoustical chamber suitable for use with oscillators of 0.933 cm cross section was, therefore, constructed. Although of more conventional design it has been diagrammatically illustrated in Fig. 4. The micrometer head A serves to determine the displacement of the polished glass reflecting surface B. The two are connected by means of an "invar" steel rod C, uncertainties in contact being prevented by the nichrome springs DD'. The rod passes through a packing of asbestos and graphite at F. Since this packing is not wholly gas-tight, an outer jacket G, which is kept at a pressure below that in the acoustical chamber, is

necessary to prevent contamination of the nitrogen tetroxide. Any nitrogen tetroxide lost by diffusion is automatically replaced from a mechanically agitated reservoir. The oscillator H is supported vertically on its dynamical center by means of a suitably fitted tungsten rod. The smallest oscillators gave, however, satisfactory results if laid on their sides horizontally without further support. The chamber itself was made of Pyrex glass, and the male member of the ground union at F of nichrome steel. Phosphoric acid served as a cement. The acoustical chamber was thermostated in a bath of transformer oil.

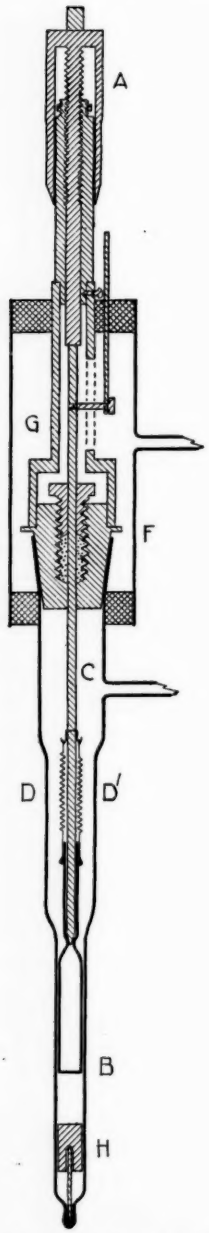

FIG. 4. Apparatus for measuring the velocity of sound in a corrosive dissociating gas at frequencies above 100 kc.

This apparatus functioned satisfactorily from 92 to 451 kc and probably would have served even to higher frequencies had this been necessary. It was used only at 30.0°C in order to avoid the construction of an elaborate thermostat, and because at this temperature all necessary information had been obtained. With suitable precautions the reproducibility obtainable with this apparatus was fully as great as that described in the preceding section. Two oscillators of different frequencies in separate acoustical chambers were invariably used with each filling of gas, and the difference between the two observed velocities was, therefore, almost independent of small quantities of accidentally included impurities.

The tube-correction in this apparatus was somewhat larger owing to its small diameter. It was determined with three nondissociating gases as indicated by Table II. Here also the sign and magnitude of the correction accords with that to be expected from the Helmholtz-Kirchhoff theory. A tube-dispersion of 0.8 m·sec.$^{-1}$ is evidently to be expected with nitrogen tetroxide in this apparatus.

TABLE II. *Determination of the tube-correction for 94 and 451 kc 0.93 cm oscillators at 30°C in a 1.0 cm glass acoustical chamber.*

Gas	P mm	V_{94} m·sec.$^{-1}$	V_{451} m·sec.$^{-1}$	$V_{451}-V_{94}$
Air	760	348.6	350.4	1.8
	760	348.5	350.3	1.8
	240	348.5	350.3	1.8
Propane	760	251.8	252.8	1.0
	760	251.7	252.8	1.1
Pentane	183	191.2	191.9	0.7
	187	191.1	191.8	0.7

Measurements of the velocity of sound in nitrogen tetroxide

Measurements on nitrogen tetroxide were confined to isobaric or isothermal lines. Those at 260 mm are summarized in Table III, and those in which the pressure was varied in Table IV. In both cases the method of presentation is the

same; the sound velocities recorded have been fully corrected, and are those used for calculations in the succeeding section. The corrections applied were: 9 kc, +0.4 m·sec.$^{-1}$; 92 kc, 0; 94 kc, +0.6 m·sec.$^{-1}$; 451 kc, −0.2 m·sec.$^{-1}$. If these are algebraically subtracted from the various velocities quoted the actual experimental velocities will be obtained. It is encouraging to note that an independent concordant determination of the tube-correction results from these measurements.

TABLE III. *The temperature dependence of the velocity of sound of various frequencies in nitrogen tetroxide at 260 mm pressure.*

T°C	Linear frequency (kc)	Velocity (m·sec.$^{-1}$)	Linear frequency (kc)	Velocity (m·sec.$^{-1}$)	Corr. $V_\omega - V_0$
1.0	9.265	170.8	92.07	172.8	1.8
1.0	9.341	171.4	92.14	173.0	
7.0	9.343	176.4	92.07	177.2	0.8
8.0	—	—	92.06	178.3	
8.1	9.340	177.5	—	—	0.8
10.0	9.331	179.2	92.02	179.9	0.7
13.9	9.336	183.05	92.00	183.6	0.55
25.0	9.298	195.3	91.89	195.7	0.3
25.0	9.298	194.8	91.89	195.0	
30.0	9.213	202.4	91.73	202.6	0.2
30.0	94.00	201.5	450.7	205.8	3.5
	94.00	201.4	450.7	205.7	3.4
	94.00	201.6	450.7	205.6	3.3

TABLE IV. *The pressure dependence of the velocity of sound in nitrogen tetroxide at various frequencies and temperatures.*

P_{mm}	Frequency (kc)	Velocity (m·sec.$^{-1}$)	Frequency (kc)	Velocity (m·sec.$^{-1}$)	Corr. $V_\omega - V_0$
		30.0°C			
342	94.00	197.8	450.7	200.9	2.3
260	94.00	201.5	450.7	205.6	3.4
235	94.00	202.8	450.7	208.1	4.5
		25.0°C			
668	9.301	184.8	91.89	185.3	0.1
260	9.301	194.7	91.89	195.4	0.3
162	9.301	201.6	91.89	202.5	0.5
		1.0°C			
260	9.340	170.7	92.10	172.9	1.8
156	9.340	175.0	92.10	179.1	3.7
132	9.340	176.3	92.10	181.0	4.3

Although the reproducibility of measurements is shown by Tables I and II to be about ±0.05 m or ±0.03 percent, the measurements in Tables III and IV are scattered over a much wider range of ±0.3 m·sec.$^{-1}$ or ±0.15 percent, and the difference between high- and low-frequency velocities cannot be read from a smoothed curve to better than ±0.1 m·sec.$^{-1}$ with confidence. This is not due to uncertainties concerning frequency, since it was measured after each experiment to ±0.05 percent. The variability of frequency shown by the 9 kc oscillator in Table III is real and not a matter of experimental uncertainty. Since each velocity quoted in Table III is, with one or two exceptions, the result of a series of measurements on a separate filling of the apparatus, it is probable that slight variations in the composition of the nitrogen tetroxide are responsible for the lack of reproducibility. Small quantities of air and nitric acid, which are involuntarily included or released from the extensive glass and metal surfaces of the apparatus are indicated as a reasonable explanation.

INTERPRETATION OF THE MEASUREMENTS IN TERMS OF DISSOCIATION RATE

Calculation of the velocity of sound at low frequency

The application of (8) to the interpretation of the velocity of sound in a real dissociating gas involves the justification of a number of assumptions and approximations. It has been supposed, to name a few of these, that the wave is plane, its amplitude small, and its form purely sinusoidal. The dissociating gas has been supposed to be perfect, non-absorbing, and non-conducting to heat. The second equation of (3) neglects the influence of temperature and pressure on the degree of dissociation. No one of these approximations is easy to justify on direct experimental grounds, and together they may conveniently be treated only by the comparison of the measured velocity of sound at low frequencies with that calculated from (8) when ω and ϑ are both negligible. This comparison is made in Table V.

In order to calculate the velocity of sound at low frequencies from (8) values for the dissociation heat, dissociation constant at constant volume, average heat capacity at constant volume, and density of the gas at various pressures and temperatures are necessary. The dissociation heat is given by Verhock and Daniels[14] as 14.6 kg·cal. and by Bodenstein[15] as 13.0 kg·cal. An error of

[14] Verhock and Daniels, J. Am. Chem. Soc. **53**, 1250 (1931).
[15] Bodenstein, Zeits. f. physik. Chem. **100**, 68 (1922).

1 kg·cal. in this quantity causes an error of about 0.4 percent in the velocity of sound calculated at low frequency, too high a dissociation heat yielding, of course, too low a velocity. For the sake of consistency 14.6 kg·cal. will be used throughout the remainder of this communication. Verhock and Daniels give the dissociation constant at 25°C and at 35°C, and at 30° a satisfactory value has been obtained by the van't Hoff isochore. The average heat capacity at constant volume is given by the expression

$$\overline{C}_0=\frac{(2\alpha C_{NO_2}+(1-\alpha)C_{N_2O_4})}{(1+\alpha)}.$$

Since the heat capacities of the component molecules are unknown the calculation has been carried through in duplicate, using the minimum ($C_{NO_2}=6$, $C_{N_2O_4}=10$) and the maximum ($C_{NO_2}=8$, $C_{N_2O_4}=16$) values which the heat capacity may reasonably be expected to assume. The densities have been obtained at 25° and 35° and, by interpolation, at 30°C from Verhock and Daniels; at 15° and 1° they have been calculated, through the dissociation constant, from the degree of dissociation and the ideal gas laws. The observed velocity of sound at 15° has been interpolated from Table III.

It is considered that the agreement obtained in Table V is sufficiently good, in view of the uncertainties in the data upon which the calculated values are based, to justify the approximations in (8) for nitrogen tetroxide at 260 mm. It is noteworthy that γ_0 is almost independent of temperature at constant pressure, and not greatly sensitive either to the value of $\overline{C}_0$ or the dissociation heat. Since P is fixed by the nature of the experiments it follows that a large part, at least, of the deviation of calculated and observed velocities must be due to uncertainties concerning the density.

The agreement at higher pressures is unsatisfactory, owing probably to failure of the ideal gas laws. The measurements at lower pressures will be discussed below.

Calculation of the reaction rate constants

The agreement of measured and calculated velocities of sound at very low frequencies removes a large number of objections from the use of (9) to evaluate dissociation rate constants. The fundamental reasoning underlying (8) from which (9) is derived should be in general valid at any frequency, for the characteristics of the gaseous system are unaltered by the sound wave. All the approximations necessary for the calculation of the velocity of sound at very low frequency are then equally justified at high frequency save only those concerning tube-dispersion, heat capacity and absorption. In view of the extended discussion in the introduction concerning the first two of these, it will be sufficient here to show that the rate constants obtained under various conditions are harmonious. That absorption must increase in the region of dispersion is implied by (2) and that it may alter the velocity appreciably follows from (8) when β^2 is not negligible with respect to ω^2/V^2. Since no means by which an irreproachable numerical magnitude may be assigned to the absorption coefficient is at present available it is believed preferable to explore the region in which the velocity of sound is close to that at very low frequency, rather than to attempt corrections for absorption at high frequencies.

The absorption coefficients obtained by measuring the mass reaction of the gas on the electrical circuit do not at present appear worthy of great confidence. The main kinetic conclusions which

TABLE V. *Comparison of observed and calculated velocities of sound in N_2O_4 at 260 mm and low frequency.*

T°C	K_p l·atm.	α	$\rho\times10^4$ g·cm^{-1}	Estimated $\overline{C}_0$ cal·deg.$^{-1}$	γ_0	Calc. V_0 m·sec.$^{-1}$	Obs. V_0 m·sec.$^{-1}$
30.0	0.2025	0.3591	9.32	11.77 7.88	1.081 1.086	200.5 201.0	202.4
25.0	0.1344	0.2991	9.94	12.31 8.16	1.080 1.086	194.1 194.6	195.1
15.0	0.0572	0.2003	11.10	13.33 8.67	1.078 1.085	183.5 184.1	184.2
1.0	0.0155	0.1058	12.66	14.47 9.24	1.078 1.087	171.8 172.5	171.1

are reached in this communication are based on differences between the velocity of sound at 9 and 92 kc, where the dispersion is small, and are believed independent of error due to absorption. The error in the rate constant due to neglecting absorption is in any case partly neutralized by that due to neglecting the tube-correction change when the dispersion is large.[16]

Two further points should be mentioned before (9) is applied to the calculation of rate constants. The quantity k_1 is defined as the number of associated molecules decomposing per second divided by the total number present. This will be a constant in the chemical sense only if the reaction is unimolecular, that is, if k_1 is independent of pressure. The sense of the dispersion theory of sound demands only that k_1 be independent of frequency. When k_1 diminishes with diminishing pressure a bimolecular or a quasi-unimolecular reaction is indicated: This will cause no difficulty in the theoretical treatment, and will indicate merely that the chemical characteristics of the reaction are not what it was simplest to assume.

A glance at (9) will show that k_1 is determined only by the differences between squared velocities, two of which are measured and the third of which, V_∞, must be calculated. Since a part of the heat capacity will almost certainly not participate in the adiabatic cycle at very high frequencies even if it remains active at frequencies where the chemical reaction begins to fall out, it appears unwise to attempt the measurement of V_∞. In the calculations which are reported below V_∞ has been considered an ideal quantity which is defined by $V_\infty=(V_0\gamma_\infty/\gamma_0)^{1/2}$ when the ratios γ_0 and γ_∞ are calculated from (8) for the real case $\omega\doteq 0$, $\overline{C}+\overline{C}_\omega=\overline{C}_0$, and for the ideal case $\omega\doteq\infty$, $\overline{C}+\overline{C}_\omega=\overline{C}_0$, respectively. This definition is justified only when k_1 as defined by (9) has been proved independent of frequency within limit of error. When permissible it has the advantage of further diminishing uncertainties in k_1 due to changes in heat capacity with frequency, and of almost wholly eliminating errors in k_1 due to failure of the ideal gas laws, or uncertainties concerning density and exact absolute velocity at very low frequency.

The rate constants obtained from (9) in the manner described above are collected in Table VI. The difference $V_\omega-V_0$ is obtained from experiment at 1° and at 30°, and has been interpolated at 15° from a plot of these differences given in Table III against temperature. The necessary values of α, γ_0, and $\overline{C}_0$ (which has been used with its maximum and minimum values as before) are quoted in Table V for the appropriate temperatures.

The accuracy of the rate constants in Table VI must now be considered. It may be shown from these by (9) that the velocity of sound at very low frequencies at 1°C is less than 0.1 m·sec.$^{-1}$ below that quoted at 9 kc. Error from this cause, is,

TABLE VI. *The dissociation rate constant of nitrogen tetroxide at 260 mm.*

T°C	$V_\omega-V_0$ m·sec.$^{-1}$	Linear frequency kc	Estimated $\overline{C}_0$ cal·deg.$^{-1}$	Ideal V_∞ m·sec.$^{-1}$	$k_1\times10^{-3}$
30.0	3.4	450.7	11.77	208.5	63
			7.88	215.8	70
30.0	0.2	91.9	11.77	208.5	70
			7.88	215.8	66
15.0	0.5	92.0	13.33	189.7	26
			8.67	195.5	26
1.0	1.8	92.1	14.47	175.3	6.3
			9.42	180.5	7.7

[16] The absorption of sound in a dissociating gas has recently been suggested by Luck (Phys. Rev. **40**, 440 (1932)) as a means of determining dissociation rates. Absorption is discussed in some detail from the standpoint of Einstein's theory in his communication. Recent comment by Teeter (J. Am. Chem. Soc. **54**, 4111 (1932)) on the advance notice of this work necessitates a brief addition. The velocity of sound as determined above involves the examination of relatively few wave-lengths, which are chosen near the source to avoid possible effects of radial resonance. Under these conditions a small increase in the absorption coefficient at the edge of the dispersive region passes unnoticed. The absorption coefficient enters Einstein's expression for the velocity in the second approximation, but when the dispersion is small its effect on the calculated rate constant may be neglected in view of other uncertainties of calculation and experiment. In the center of the (first) dispersive region the correction due to absorption becomes considerable but there, for other reasons, acceptable values for the rate constant cannot at present be obtained. Absorption coefficients for the intensity may easily be evaluated by means of the velocities here reported and the expression given by Luck for the amplitude coefficient, but it is felt that their present value is small since their connection with any measurable quantity is not clear. The effect of absorption on the measured velocity of sound is also believed to require more detailed treatment than it has at present received, and references above to the interrelation of the two are intentionally vague.

therefore, eliminated. The rate constant obtained at 30°C and 91.9 kc is open to objection on the ground that 0.2 m·sec.$^{-1}$ is scarcely greater than experimental error for the quantity $V_\omega - V_0$; it is nevertheless considered significant because it coincides with that obtained by extrapolation from $V_{92} - V_9$ at lower temperatures by the use of an experimentally determined activation energy. The coincidence of the rate constant from measurements at 30° and 450.7 kc with that at lower frequencies is well within experimental error, and must be considered accidental. A detailed examination of the various sources of error leads to the conclusion that accuracy better than 10 percent cannot be claimed for the rate constants in Table VI, and that experimental uncertainties in the quantity $V_\omega - V_0$ are of more importance than uncertainties in the thermodynamic properties of nitrogen tetroxide.

If precise data for comparison with these rate constants were available the research would not have been undertaken. The highest published lower limit for the reaction rate set by the acoustical method is 5×10^4 at 25° and 250 mm[4], which agrees reasonably well with the positive constant 4.8×10^4 resulting from these experiments. Brass and Tolman[17] by a quite different method have obtained positive evidence of the dissociation rate which indicates the limits of 2.4 to 8.4×10^4 at 25°, a conclusion which is in accord with the result here supported.

The activation energy of dissociation

The activation energy required by the dissociation process is easily obtained by the Arrhenius isochore from the rate constants in Table VI. Between 1° and 15° this is 15.7 kg·cals. if the "maximum" heat capacity is used and 13.6 kg·cals. using the "minimum." An uncertainty of 0.1 m·sec.$^{-1}$ in $V_\omega - V_0$ at either temperature would alter these values about 1 kg·cal. The activation energy appears to be 13.6 to 13.2 kg·cals. from the measurements at 1° and 92 kc and at 30° and 451 kc; this is far less sensitive to slight errors in $V_\omega - V_0$ than the preceding values. A survey of all the various activation energies obtainable from these experiments and all sources of error leads to the average value 13.9 ±0.9 kg·cals. Since this agrees well with estimates of the dissociation heat (13.0 to 14.6 kg·cals.) it may reasonably be supposed that the activation energy for the association of two nitrogen dioxide molecules is small.

[17] Brass and Tolman, J. Am. Chem. Soc. **54**, 1003 (1932).

The order of the dissociation reaction

If k_1 is independent of pressure the dissociation reaction may be considered unimolecular; if it depends directly on pressure it may be considered bimolecular. The rate constants obtained by applying (9) to the measurements in Table IV are given in Table VII. Some increase in the dispersion of sound with decreasing pressure is of course to be expected from the increased dissociation of the gas.

The interpretation of these measurements is less secure than the interpretation of those used to obtain the activation energy, for several uncertainties eliminated at 260 mm reappear as possible sources of error at pressures other than this. Chief among these is the heat capacity, which is particularly important when the dispersion is large. Any conclusion based on Table VII must, therefore, be tentative. It appears that the rate constant decreases with pressure, particularly at low pressures, and this effect is believed to be real although the course of k_1 with P may not be precisely indicated by Table VII.

The Kinetics of Dissociation and Association

If the interpretation given in the last section of the velocity of sound in nitrogen tetroxide is accepted it may be supposed that the dissociation process has an activation energy of 14 kg·cal., and a rate constant of 4.8×10^4 at 25°C and 260 mm. It may further be granted that the rate constant varies somewhat with pressure, at least below about 300 mm at this temperature, and that the activation energy is equal to the dissociation heat. With these data it is possible, by the application of standard relationships, to form a reasonably clear kinetic picture of the reaction.[18]

The number of nitrogen tetroxide molecules decomposing cc^{-1} sec.$^{-1}$ is $k_1 n_1$, and at 25°C and

[18] The kinetic formulae employed have been adapted from the article by Herzfeld and Smallwood in Taylor's *Treatise on Physical Chemistry* (Van Nostrand) 1931, and from Kassel's Monograph, *The Kinetics of Homogeneous Gas Reactions*, (Chem. Cat. Co.) 1932.

TABLE VII. *Variation of the velocity constant of dissociation with pressure at various temperatures.*

T°C	Pmm	n_1+n_2 $\times10^{-18}$	n_1 $\times10^{-18}$	Estimated $\overline{C}_0$ cal·deg.$^{-1}$	Ideal V_∞ m·sec.$^{-1}$	$k_1\times10^{-3}$
30.0	342	10.97	6.61	12.16	205.9	72
				8.07	212.3	78
30.0	260	8.34	3.94	11.77	208.5	63
				7.88	215.8	70
30.0	235	7.54	3.41	11.62	211.5	49
				7.81	218.5	60
25.0	668	21.79	15.09	13.53	190.4	61
				8.76	196.3	60
25.0	260	8.48	4.58	12.31	201.9	49
				8.16	208.0	47
25.0	162	5.28	2.41	11.63	210.2	45
				7.90	216.6	43
1.0	260	9.02	7.29	14.47	175.3	6.3
				9.24	180.5	7.2
1.0	156	5.53	4.21	14.08	180.2	4.2
				9.04	185.8	6.1
1.0	132	4.68	3.47	13.93	181.6	3.4
				8.97	187.2	5.6

260 mm is evidently 2.2×10^{23}. Assuming cross-sections $\sigma_1=5.3\times10^{-8}$ and $\sigma_2=4.2\times10^{-8}$ cm, the number of double collisions suffered by nitrogen tetroxide molecules is

$$Z_{11,\,12}=2n_1^2\sigma_1^2\left(\frac{\pi RT}{M_1}\right)^{1/2}+2n_1n_2\left(\frac{\sigma_1+\sigma_2}{2}\right)^2\left[\left(\frac{M_1+M_2}{M_1M_2}\right)2\pi RT\right]^{1/2}$$

when M_1 and M_2 refer to molecular weights. $Z_{11,\,12}$ is, therefore, 9.1×10^{27} cc^{-1} sec.$^{-1}$. The fastest rate at which the dissociation reaction may proceed is given by

$$k_1n_1=Z_{11,\,12}\,e^{-E/RT}\sum_{m=0}^{m=\frac{1}{2}s-1}\frac{1}{m!}\left(\frac{E}{RT}\right)^m$$

where s is the number of classical squared terms which contribute to the internal heat capacity. If s is taken as 12 to 13 agreement is obtained with the measured reaction rate within limit of error. Experiment, however, excludes a value as large as this. It will be seen from Tables IV and VII that at 1°C and 132 mm the measured velocity of sound at 92 kc is within 0.6 m·sec.$^{-1}$ of the idealized velocity at infinite frequency if this is calculated on the basis that $C_{N_2O_4}=16$. Even granting considerable uncertainty in the significance of this measurement it appears unlikely, from the way in which the dissociation work must disappear as the pressure is lowered, that a higher value for the heat capacity at 1°C is permissible. Very similar conclusions may be drawn from the corresponding values at 30.0° and 235 mm in the same tables. Hence, at 25°, the maximum dissociation rate permissible with normal cross sections would appear to be

$$9.2\times10^{27}\times10^{-10}(23.5^4/4\,!)+(23.5^3/3\,!)=2.2\times10^{22}\text{ molecules cc}^{-1}\text{ sec.}^{-1}$$

which is inferior to the measured value. If the responsibility for this discrepancy is attributed to the cross section chosen, it is necessary to suppose $Z_{11,\,12}$ larger by about one order of magnitude, and hence to increase the kinetic cross sections by about three-fold. This result finds an analogy in the behavior of nitrogen pentoxide. The heat capacity of nitrogen pentoxide is not, however, known even to the rough approximation employed above, and hence the limit to the number of vibrational terms which may be supposed active is more flexible.

The rate of the association reaction is less illuminating. If it is supposed that the association reaction occurs by suitable triple collisions, the number of which is $Z_{112,\,111}/Z_{22,\,12}=\sigma_2/\Lambda$ where Λ, the mean free path, is defined as

$$\frac{1}{\Lambda}=\pi(2)^{1/2}n_2\sigma_2^2+\pi n_1\left(\frac{\sigma_1+\sigma_2}{2}\right)^2\left(\frac{M_1+M_2}{M_1M_2}\right)^{1/2}$$

there is obtained, using normal kinetic cross sections, $\sigma_2/\Lambda=3.6\times10^{-3}$ and $Z_{111,\,112}=2.8\times10^{25}$. Calling ϵ the fraction of all triple collisions which are effective it follows that $Z_{111,\,112}\,\epsilon=(k_1/K)n_2$ and $\epsilon=5.0\times10^{-2}$. The association reaction requires no activation energy, and consequently, might be expected to occur on every suitable triple collision. The value of ϵ indicates that this is roughly the case, but little significance may safely be attributed to this coincidence since nothing is known concerning the steric factor or directional specificity of the collision process, and the duration of the triple collision is ill-defined. Furthermore, a certain number of association reactions are now known which do not appear to require a third body. In view of these uncertainties it is considered unwise to base definite conclusions on the rate constant of the association reaction.

The large molecular diameters which it is necessary to assume for the activation process raise at once the question of the effectiveness of various types of collision in provoking dissociation. An expression for the velocity of sound in a mixture of gases one of which is dissociating has been developed, and a few observations already collected dealing with this matter. They are not included here because it is felt that this communication, even when confined to a pure dissociating gas, is excessively long and detailed. It is hoped that conclusions along these lines, and also a report of the extension of the acoustical method to other dissociating gases may be presented for publication in the near future.